

**Coating method utilizing a polymer film and method of making metal-polymer laminates**

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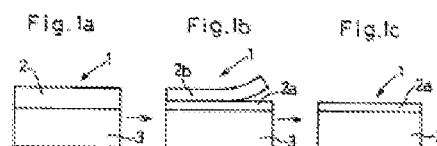
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A coating layer of a polymer capable of forming an optically anisotropic melt phase is formed by heat-pressing to a base material a film made of the polymer and having a segment orientation ratio of not greater than 1.3 and then separating the film into two halves so as to leave one of the halves on the base material, thereby obtaining a coated material made of the base material and the thin coating layer.



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## Coating method utilizing a polymer film and method of making metal-polymer laminates

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[0001] The present invention relates to a coated material having an isotropic coating layer that is obtained by peeling a portion of a film press-fitted to a base material such as a metal foil and made of a polymer capable of forming an optically anisotropic melt phase, and a method of making the coated material. The present invention also relates to a metal-polymer laminate obtained by peeling a portion of the polymer film firmly sandwiched between metal foils, in a direction thicknesswise thereof, and a method of making the metal-polymer laminate.

[0002] In the description of the present invention, the polymer capable of forming an optically anisotropic melt phase is referred to as a "liquid crystal polymer"; the film made of the liquid crystal polymer is referred to as a "liquid crystal polymer film"; and the coated material is intended to mean an article of manufacture formed with the liquid crystal polymer coating layer by coating the liquid crystal polymer to the base material.

[0003] The liquid crystal polymer has been well known which has various advantageous features including (1) a capability of being thermally bonded directly to a metallic foil layer; (2) a high resistance to heat; (3) a low moisture absorptivity; (4) an excellent dimensional stability to thermal change in size; (5) an excellent resistance to change in size brought about by moisture; (6) an excellent property in high frequency characteristic; (7) a fire-proof property with no need to add a flame retardant containing a toxic halogen, phosphorus, antimony and others; (8) an excellent resistance to chemicals; (9) an excellent resistance to radiations; (10) having a controllable thermal expansion coefficient; (11) a flexibility at low temperatures; (12) a property of a high gas barrier (a considerably low permeability to a gaseous material such as, for example, oxygen), and so on.

[0004] In recent years, demands have been arisen to use such excellent liquid crystal polymer as a coating material to be applied in the form of a thin film to a metallic foil layer, a silicon plate or a ceramics plate to provide a base material for a precision circuit substrate, a multi-layered circuit substrate, a sealing material or a package can. In addition, because of the resistance to heat and chemicals, the low moisture absorptivity and the gas barrier property, demands have increased for the use of the liquid crystal polymer as a coating material that can be utilized to form a protective layer on a metal susceptible to corrosion.

[0005] The first problem in utilizing the liquid crystal polymer as a coating material will first be discussed:

[0006] To form a thin skin film of, for example, a synthetic resin over the surface of an article of manufacture, various methods have been known such as, for example, a lining process and a coating process. The lining process and the coating process are known to be distinct from each other because of the following reasons. Specifically, the coating process has a primary objectivity in decorative purpose to form a continuous skin film over the article to thereby protect the article from corrosion and contamination and also to provide the article with an appealing ornament and is also often used to form a film for imparting a non-adhesive property and a low frictional property. On the other hand, the lining process is a process of forming a protective thick film on vessels (baths) and tubes or pipes that are used in the chemically and/or physically severe environment where corrosion and/or erosion are strictly desired to be avoided. However, the coating and lining processes have features so common to each other that the line of distinction can hardly be drawn therebetween. It is generally recognized that the skin layer having a thickness of 0.5 mm or more is classified as a lining whereas the skin film having a thickness of 0.5 mm or less is classified as a coating. It is also generally recognized that the coating is to form a film of several tens microns mainly on a surface of a structure whereas the lining is to form a film of several hundreds microns.

[0007] In either case, the present invention pertains to a technique of forming on a base material a very thin film of a liquid crystal polymer to a thickness of 25  $\mu\text{m}$  or less, particularly 15  $\mu\text{m}$  or less and may therefore be said to pertain to the coating technique.

[0008] As one of important properties of the coating, attention is centered on the durability of the coating against change in temperature and, however, this leads to a problem of how the difference in thermal expansion coefficient between the coating and the base material bearing the coating should be resolved. While the coating process includes, inter alia, (1) a dipping method, (2) a flow coating method, (3) a curtain coating method, (4) a roll coating method, (5) an electro-deposition method, (6) a brush coating method, (7) a spray coating method and (8) a gas-phase coating method, none of these known methods can be utilized to form a film of a liquid crystal polymer by the following reason. Specifically, due to a unique property of the liquid crystal polymer in that molecules of the liquid crystal polymer have a propensity of orienting in the same direction, the liquid crystal polymer molecules tend to be oriented in the same direction when a force is applied to a molten liquid crystal polymer being applied to form a thin film. Considering that the physical property such as thermal expansion coefficient measured in a direction conforming to the molecular orientation is considerably different from that measured in a direction transverse to the molecular orientation, that is, the liquid crystal polymer has an anisotropy, it is impossible to render the coating-bearing base material and the layer of the liquid crystal polymer to have the same or substantially same thermal expansion coefficient in all directions on a plane. Although the prior art coating process is capable of providing a liquid crystal polymer layer of a large thickness of, for example, 50  $\mu\text{m}$  or more, it has been found that the resultant liquid crystal polymer layer has an anisotropy and is therefore incapable of being used as a practically utilizable coating. Nonetheless, no technique of forming a layer of a liquid crystal polymer having an improved isotropy to a thickness of 15  $\mu\text{m}$  or less have hitherto been made available.

[0009] The second problem will now be discussed:

[0010] Circuit substrates or the like that are generally utilized in the field of electronics make use of a metal-

resin laminate prepared by press-bonding together a foil layer of an electroconductive metal and a film-like insulating material (a film or a sheet with or without a metallic foil layer coated thereon) having an electrically insulating property. The metal-resin laminate is available in the form of a double-sided metal-resin laminate in which an electric insulating layer is sandwiched between two metallic foil layers and of a single-sided metal-resin laminate in which a single metallic foil layer and a single electric insulating layer are bonded together. The liquid crystal polymer having the excellent properties as discussed above is generally recognized as an ideal material for the electric insulating layer used in the laminates.

[0011] As a method of making a metal-polymer laminate without diminishing the excellent properties of the liquid crystal polymer, various methods have been well known. (i) Specifically, in the case of the double-sided metal-polymer laminate, the method is known to comprise sandwiching a liquid crystal polymer layer between two metallic foil layers, and hot-pressing the resultant sandwich structure with the use of a hot plate or a hot roll to cause the liquid crystal polymer to melt so that the metallic foil layers and the liquid crystal polymer layer can be thermally bonded together to eventually provide the double-sided metal-polymer laminate upon solidification of the liquid crystal polymer. (ii) On the other hand, in the case of the single-sided metal-polymer laminate, the method is known to comprise sandwiching a liquid crystal polymer layer between a single metallic foil layer and a single release film, hot-pressing the resultant sandwich structure with the use of a hot plate or a hot roll to cause the liquid crystal polymer to melt so that the metallic foil layer and the liquid crystal polymer layer can be thermally bonded together, and removing the release film to leave the resultant single-sided metal-polymer laminate.

[0012] While the prior art method of making the double-sided metal-polymer laminate is satisfactory, the prior art method of making the single-sided metal-polymer laminate has a problem in that since the release film has to be removed and is then discarded, manufacture of the single-sided metal-polymer laminate tends to be costly. Moreover, since a high temperature of about 300 DEG C is required to melt the liquid crystal polymer in the practice of making the single-sided metal-polymer laminate, the release film used must be chosen from highly heat-resistant films made of an expensive resinous material such as, for example, Teflon TM or polyimide, and increase of the manufacturing cost brought about by the use of the expensive release film has made it very difficult to manufacture the single-sided metal-polymer laminate on a commercially profitable basis.

[0013] On the other hand, demand has arisen particularly from electronics concerns for availability of circuit substrates having a more reduced thickness. Since as discussed hereinabove the liquid crystal polymer is suited as a material for the electric insulating layer, realization of a circuit substrate comprising a thin layer of the liquid crystal polymer and a thin foil layer of metal is persistently longed for.

[0014] Although a film of the liquid crystal polymer is often required for the thin liquid crystal polymer layer, the liquid crystal polymer film if manufactured in a usual manner would have a molecular orientation dominantly in one direction. The film having the molecular orientation dominantly in one direction tends to be easily torn in a direction parallel to the molecular orientation and also tends to exhibit considerably differing thermal changes in shape in respective directions parallel to and transverse to the molecular orientation, that is, to exhibit an anisotropic film. Therefore the liquid crystal polymer hitherto available in the market can hardly be used as a material for the electric insulating layer in the circuit substrate. However, as discussed in connection with the first problem, it is difficult to form a film having a thickness of 15  $\mu\text{m}$  or less with an isotropic liquid crystal polymer for use as a material for the electric insulating layer, and much difficulty has hitherto been encountered to form a film having a thickness of 10  $\mu\text{m}$  or less. No report has hitherto been made yet which show a success in making the isotropic liquid crystal polymer film having a film thickness not greater than 10  $\mu\text{m}$ .

[0015] Accordingly, the present invention has been devised with a view to substantially eliminating the above discussed first problem inherent in the prior art coating methods and is intended to provide a means for forming the liquid crystal polymer coating, particularly the liquid crystal polymer coating having a reduced thickness, in which a problem associated with the anisotropic molecular orientation is resolved, that is, having an improved isotropy to thereby substantially eliminate the first problem discussed hereinbefore.

[0016] Another important object of the present invention is to provide an improved method of making the single-sided metal-polymer laminate in which no release film is required, to thereby substantially eliminate the second problem discussed hereinbefore.

[0017] A further important object of the present invention is to provide an improved laminate comprising a metallic foil layer and an electric insulating layer prepared from the liquid crystal polymer from which a problem associated with the anisotropic molecular orientation is resolved.

[0018] According to the coating method of the present invention, a film prepared from a liquid crystal polymer and having a segment orientation ratio (SOR) of not greater than 1.3 is hot-pressed and, hence, bonded to a base material to provide a layered structure. The liquid crystal polymer film is subsequently peeled off from the layered structure so as to leave a thin ply of the liquid crystal polymer on the base material. In this way, a thin liquid crystal polymer coating can easily be obtained.

[0019] A coated material having a thin coating of the liquid crystal polymer left on the base material according to the present invention comprises a coating of the liquid crystal polymer capable of forming a melt layer having an optically anisotropy, in which the segment orientation ratio of the liquid crystal polymer coating is not greater than 1.3. In a preferred embodiment of the coated material of the present invention, the coating layer referred to above has a thickness not greater than 15  $\mu\text{m}$ . Accordingly, the coating in the coated material of the present invention has an isotropic molecular orientation while securing a small thickness, and therefore, the coated material of the present invention can advantageously be used as a material for the precision circuit substrates, the multi-layered circuit substrates, sealing members, package cans with maximized utilization of the excellent properties of the liquid crystal polymer discussed hereinbefore.

[0020] The term "segment orientation ratio" used hereinbefore and hereinafter is an index descriptive of the

degree of orientation of molecules forming a segment and represents, unlike the standard MOR (molecular orientation ratio), a value in which the thickness of a object is taken into consideration. This segment orientation ratio can be calculated in the following manner.

[0021] Using a commercially available microwave molecular orientation degree measuring apparatus shown in Fig. 6 and available from the KS Systems Corporation, the intensity (the microwave penetration strength) of an electric field of the microwaves transmitted through a liquid crystal polymer film is first measured.

[0022] The measuring apparatus indicated by 61 in Fig. 6 comprises a microwave generator 63 capable of generating microwaves MVV of a predetermined wavelength that irradiate a liquid crystal polymer film 65, a microwave resonant waveguide 64 and a penetration strength detecting means 68. The microwave resonant waveguide 64 has an intermediate portion thereof at which the liquid crystal polymer film 65 is set so as to lie vertically with respect to the direction of propagation of the microwaves MVV. The liquid crystal polymer film 65 so placed is retained for rotation in the direction R in a plane perpendicular to the direction of propagation of the microwaves MVV by means of a rotary drive mechanism (not shown). The microwave resonant waveguide 64 includes a pair of reflecting mirrors 67 disposed at respective opposite ends of the waveguide 64 for reflecting the microwaves MVV penetrating through the liquid crystal polymer film 65 to allow the waveguide 64 to undergo resonance. The strength of the microwaves which have penetrated through the liquid crystal polymer film 65 can be detected by the penetration strength detecting means 68. This penetration strength detecting means 68 includes a detecting element 68a disposed at a predetermined position rearwardly within the microwave resonant waveguide 64 to measure the microwave penetration strength.

[0023] Based on the resultant measurement, a m value (hereinafter referred to as an "index of refraction") can be calculated from the following equation:  

$$m = (Z_0 / \Delta z) \times (1 - \nu_{\max} / \nu_0)$$
 wherein  $Z_0$  represents a device constant,  $\Delta z$  represents an average thickness of an object subjected to the measurement,  $\nu_{\max}$  represents the frequency at which the maximum microwave penetration strength can be obtained when the frequency of the microwaves is changed, and  $\nu_0$  represents the frequency at which the maximum microwave penetration strength can be obtained when the average thickness is zero, that is, when no object is present.

[0024] The segment orientation ratio (SOR) can be calculated from the following equation:  

$$SOR = m_0 / m_{90}$$
 wherein  $m_0$  represents a value of the m value which is exhibited when the angle of rotation of the object in a direction indicated by R in Fig. 6 relative to the direction of oscillation of the microwaves is 0 DEG, that is, when the direction of oscillation of the microwaves is aligned with the direction in which molecules of the object are most oriented and in which the minimum microwave penetration strength is exhibited, and  $m_{90}$  represents a value of the m value which is exhibited when the angle of rotation of the object in the direction R is 90 DEG.

[0025] The SOR of ideal isotropic films exhibits 1, while the SOR of a liquid crystal polymer film prepared by the use of the standard T-die film forming method and in which molecules are oriented strongly in one direction exhibits about 1.5. The SOR of the isotropic film obtained by the use of the standard isotropic inflation film forming method is not greater than 1.3.

[0026] The liquid crystal polymer includes all kinds of liquid crystal polymer such as Half-1 liquid crystal polymer, Whole-1 liquid crystal polymer, Half-2 liquid crystal polymer, and Whole-2 liquid crystal polymer. See "Seikei . Sekkei no tameno Ekisho Porimah (Liquid Crystal Polymer for Molding and Design)" authored by Junichi Suenaga and available from the Sigma Publishing Co.

[0027] In any event, examples of the liquid crystal polymer include, for example, well known thermotropic liquid crystal polyester and thermotropic liquid crystal polyester amide prepared from compounds, such as classified under (1) to (4) below, and their derivatives. It is, however, pointed out that to prepare a liquid crystal polymer, various raw material compounds have their proper combination and amount carefully chosen.

(1) Aromatic or aliphatic dihydroxy compounds, representative examples of which are shown in Table 1 below.

EMI10.1

(2) Aromatic or aliphatic dicarboxylic acids, representative examples of which are shown in Table 2 below.

EMI11.1

(3) Aromatic hydroxycarboxylic acid, representative examples of which are shown in Table 3 below.

EMI11.2

(4) Aromatic diamines, aromatic hydroxyamines and aromatic aminocarboxylic acids, representative examples of which are shown in Table 4 below.

EMI12.1

(5) Representative examples of the liquid crystal polymers prepared from any of those starting material compounds include copolymers having such structural units as indicated by (a) to (e) in Table 5 below.

EMI12.2

[0028] Those liquid crystal polymers preferably have a transition temperature to an optically anisotropic melt phase within the range of from about 200 to about 400 DEG C, more preferably from about 250 to about 350 DEG C, so that the resultant film can have a desirable heat resistance and a desirable processability. Unless physical properties of the liquid crystal polymer film are impaired, one or a mixture of

various additives such as a smoothing agent, an antioxidant and a filler may be added thereto if desired.

[0029] The film prepared from any of those liquid crystal polymers discussed above can be made by the use of one or a combination of the well-known T-die process and the well-known inflation process. Particularly with the inflation method, stresses can be applied not only in a direction of the mechanical axis of the film (which direction is hereinafter referred to as the MD direction), but also in a direction (hereinafter referred to as TD direction) perpendicular to the MD direction and, therefore, the inflation method is effective to eventually manufacture the liquid crystal polymer film having balanced physical and thermal properties in both of the MD and TD directions.

[0030] Accordingly, one of important features of the present invention lies in the use of the isotropic liquid crystal polymer film as a coating material, and even if the anisotropic liquid crystal polymer film having the segment orientation ratio (SOR) greater than 1.3 is used as a coating material and even if after this coating material has been applied, the anisotropic liquid crystal polymer coating layer is heated to melt, this will not transform into an isotropic liquid crystal polymer coating layer. This is a fundamental behavior of molecules of the liquid crystal polymer, and the inventors of the present invention have experimentally confirmed that even though the anisotropic liquid crystal polymer coating layer is heated to a temperature 35 DEG C higher than the melting point of the liquid crystal polymer, it would not transform into the isotropic liquid crystal polymer.

[0031] The base material to which the liquid crystal polymer film is applied may be made of any inorganic material such as, for example, metal, glass or ceramics, or any organic material such as, for example, plastics, wood, textile fibers, provided that those materials have a softening point higher than the temperature at which the liquid crystal polymer is fusion-bonded thereto. It is to be noted that the liquid crystal polymer itself can be included as a material for the base material. By way of example, for the purpose of improving surface characteristics (such as, for example, bondability, physical properties, frictional resistance, surface wettability, gas barrier property, resistance to chemicals, resistance to solvents, affinity to solvents, aesthetic appearance and so on) of the base material mixed with a reinforcement such as filler or glass cloth or without filler or glass cloth, the liquid crystal polymer coating layer may be provided on the surface of the base material.

[0032] In particular, the liquid crystal polymer coating layer of the present invention is suited for retention of electronic components or electronic circuits forming an electronic board and, in such cases, the metallic foil layer may often comprise the base material. Material for the metallic foil may be selected from metals of a kind used in electric connections and is preferably chosen from the group consisting of, for example, gold, silver, copper, nickel, aluminum, iron, steel, tin, brass, magnesium, molybdenum, a copper-nickel alloy, a copper-beryllium alloy, a nickel-chromium alloy, a silicon carbide alloy, graphite and a mixture thereof.

[0033] Another one of the important feature of the present invention lies in that after a film of the isotropic liquid crystal polymer has been hot-pressed to the base material, the film is peeled off from the base material so as to leave a thin film of the liquid crystal polymer on the base material. While this is difficult with ordinary polymers, this type of coating can be accomplished only when the intra-layer separability which is a unique property of the liquid crystal polymer film is utilized. The term "intra-layer separability" means a capability of the liquid crystal polymer film being internally separated to produce mica-like thin flakes of liquid crystal polymer. In order for the isotropic liquid crystal polymer film to be hot-pressed and, hence, fusion-bonded to the base material while making maximized use of the excellent intra-layer separability, the heating temperature should not be increased to a value equal to or higher than the melting point of the liquid crystal polymer.

[0034] The liquid crystal polymer coating layer so formed on the surface of the base material by the method described above may, when subsequently heated to the temperature not lower than the melting point, lose the intra-layer separability. Also, where after the liquid crystal polymer coating layer and any other material have been overlapped together in face-to-face relation with each other the base material and such any other material are hot-pressed together at a temperature not lower than the melting point of the liquid crystal polymer, no intra-layer separation occurs in the liquid crystal polymer coating layer since the liquid crystal polymer coating layer is heated to a temperature not lower than the melting point thereof during a hot-pressing process.

[0035] The coated material having the isotropic liquid crystal polymer according to the present invention has the liquid crystal polymer coating layer which preferably has a thickness not greater than 15  $\mu\text{m}$ .

[0036] The film forming method for forming the liquid crystal polymer film is one of the high-tech methods and manufacture of the thin film is difficult to accomplish without incurring an increase in manufacturing cost. In general, manufacture of the liquid crystal polymer coating layer of 20  $\mu\text{m}$  or greater is relatively easy and, depending on the circumstances, the liquid crystal polymer coating layer can be obtained by a simple manufacture which does not require a peeling process to induce the intra-layer separation. Nevertheless, it is often considered important to prepare the liquid crystal polymer coating layer of 20  $\mu\text{m}$  or greater in thickness through the peel-off process since when the thick liquid crystal polymer coating layer is internally separated by peeling off, the coating layer will have a rough surface effective to retain a bonding material.

[0037] However, the coated material according to the present invention is effectively utilized where in its application to the electronic circuit substrates and their related component parts a thin liquid crystal polymer coating layer is required. Accordingly, in order to provide the isotropic liquid crystal polymer coating layer particularly having a thickness not greater than 20  $\mu\text{m}$ , preferably not greater than 15  $\mu\text{m}$ , the coating method herein disclosed and claimed in accordance with the present invention is the sole effective method to accomplish it. With the coating method of the present invention, the liquid crystal polymer coating layer may have an extremely small average thickness, the minimum value of which is close to zero, and the liquid crystal polymer coating layer having an average thickness of, for example, 1  $\mu\text{m}$  or smaller can easily be manufactured. Under precisely controlled conditions, it is possible to manufacture the isotropic liquid crystal polymer coating layer having an average thickness of 0.1  $\mu\text{m}$  or smaller.

[0038] In the coated material having the isotropic liquid crystal polymer coating layer according to the present invention, the isotropic liquid crystal polymer coating layer and the base material on which the isotropic liquid crystal polymer coating layer is applied preferably have the same or substantially same thermal expansion coefficient.

[0039] As discussed in connection with the problems inherent in the prior art, the thermal expansion coefficient of the liquid crystal polymer coating layer is preferably as close to that of the base material as possible. In particular, if the dimensional change between the base material and the coating layer relative to a temperature change of 100 DEG C is 0.2% or less, the liquid crystal polymer coating layer can satisfactorily be used as a precise coating material for the electronics component parts. Accordingly, the fact that the thermal expansion coefficient of the isotropic liquid crystal polymer coating layer and that of the base material are substantially equal to each other speaks of  $\pm 20$  ppm/ DEG C (that is,  $\pm (2/1,000)\%$ / DEG C). Thus, the simplest method to render the thermal expansion coefficient of the liquid crystal polymer coating layer to be as close to that of the base material as possible is to make the thermal expansion coefficient of the liquid crystal polymer film, which serves as a material for the coating layer, equal to that of the base material. However, even though the liquid crystal polymer film and the base material have respective thermal expansion coefficients different from each other, heat treatment of the liquid crystal polymer coating layer formed by the use of the liquid crystal polymer film is effective to render the respective thermal expansion coefficients to be substantially equal to each other. If during the heat treatment the heating temperature is very precisely controlled, it is possible to allow the base material and the coating layer to have the respective thermal expansion coefficients which substantially match with each other within a measurement tolerance. In order to control the thermal expansion coefficient where the standard thermoplastic polymer having no liquid crystal phase or the standard thermosetting resin such as epoxy resin is employed for the coating layer, special operations are required to add an inorganic powder or an inorganic cloth to the coating layer, and to control the proportion of the additive in the coating layer or to control the cross-linking density of polymer molecules forming the coating layer. However, in the case of the liquid crystal polymer coating layer, it can easily be accomplished with the simple heat treatment owing to the unique properties of the liquid crystal polymer molecules.

[0040] As described above, the present invention makes use of the unique feature of the liquid crystal polymer in which the molecules of the liquid crystal polymer can easily be oriented and can exhibit the excellent intra-layer separability when formed into a film. Because of this, the thin liquid crystal polymer coating layer of the present invention can be easily formed by initiating the intra-layer separation when the liquid crystal polymer film hot-pressed to the surface of the base material is being peeled off from the base material, so as to leave a fraction of the thickness of the liquid crystal polymer film on the base material.

[0041] The method of making the metal-polymer laminate of the present invention which will be described subsequently is closely associated with the liquid crystal polymer coating method of the present invention in that the intra-layer separability of the liquid crystal polymer is utilized, provided that the base material in the above described liquid crystal polymer coating comprises a metallic foil.

[0042] The method of making the single-sided metal-polymer laminate according to the present invention can be practiced by separating the double-sided metal-polymer laminate, which comprises the layer of the liquid crystal polymer having its opposite surfaces bonded with upper and lower metallic foils, into first and second single-sided metal-polymer laminates. The resultant first single-sided metal-polymer laminate comprises the upper metal foil having a lower surface to which a portion of the liquid crystal polymer layer is bonded whereas the resultant second single-sided metal-polymer laminate comprises the lower metal foil having an upper surface to which the remaining portion of the liquid crystal polymer layer is bonded. Thus, with no need to use such release film hitherto required in the practice of the prior art method, not only can the single-sided metal-foil laminates be easily obtained, but also two single-sided metal-foil laminates can be obtained at a time through a single peel-off process and the speed of manufacture of the laminate is accordingly substantially twice that required to manufacture the single laminate.

[0043] In the practice of the single-sided metal-polymer laminate making method of the present invention, the double-sided metal-polymer laminate is preferably made by sandwiching the liquid crystal polymer film between two metallic foils to provide a sandwich structure which is subsequently hot-pressed by means of a hot-press. The single-sided metal-polymer laminates according to the present invention are manufactured by means of the method of the present invention described hereinabove.

[0044] The single-sided metal-polymer laminate of the present invention includes the liquid crystal polymer layer having a thickness preferably not greater than 15  $\mu$  m. Also, the liquid crystal polymer layer in the single-sided metal-polymer laminate of the present invention has a segment orientation ratio (SOR) which is preferably not greater than 1.3.

[0045] The parts-mounted circuit board of the present invention makes use of the above described single-sided metal-polymer laminate on which electronic component parts are mounted and connected electrically.

[0046] The multi-layered parts-mounted circuit board of the present invention is of a structure in which the single-sided metal-polymer laminate of the present invention is laminated with a similar single-sided metal-polymer laminate or any other laminate, and electronic component parts are mounted on at least one surface of the multi-layered parts-mounted circuit board.

[0047] In the practice of the method of making the double-sided metal-polymer laminate according to the present invention, a metal foil is applied to and is then hot-pressed to one of opposite surfaces of the liquid crystal polymer layer of a single-sided metal-polymer laminate remote from the metal foil to thereby complete the double-sided metal-polymer laminate. The double-sided metal-foil laminate of the present invention is manufactured in this manner.

[0048] The apparatus for making the single-sided metal-polymer laminate according to the present invention comprises a hot-press device for hot-pressing the liquid crystal polymer film sandwiched between first and second metal foils in a layered structure in a direction across the thickness of the liquid crystal

polymer film, and a separating device for separating the resultant double-sided metal-polymer laminate into first and second single-sided metal-polymer laminates along a plane intermediate of the thickness of the double-sided metal-polymer laminate.

[0049] As hereinbefore discussed, one of the important features of the present invention lies in the utilization of the intra-layer separability owned by the liquid crystal polymer layer, that is, the capability of the liquid crystal polymer layer being separated internally into two polymer plies, so that the intended single-sided metal-polymer laminate can be obtained without allowing the unique intra-layer separability to be lost during the manufacture thereof. For this purpose, it is essential that the liquid crystal polymer layer even though softened is not caused to melt and, therefore, the temperature of the liquid crystal polymer layer should not exceed the melting point thereof. However, the liquid crystal polymer layer does not always has a fixed melting point, and the melting point thereof may vary depending on the thermal history applied to the liquid crystal polymer layer. By way of example, if the liquid crystal polymer film or layer is placed in the atmosphere of a temperature close to, but lower than the melting point thereof (for example, consistently in the atmosphere of a temperature lower by 15 DEG C than the melting point thereof), the melting point at the starting time will increase with time and will finally increase to a value higher by about 120 DEG C than the melting point thereof at the starting time. Thus, at the time the melting point of the liquid crystal polymer film or layer has increased to the temperature higher than that at the starting time, the intra-separability of the liquid crystal polymer film or layer will not be lost provided that it is heated to a temperature lower than the increased melting point thereof.

[0050] In the practice of the present invention, the hot-pressing may be carried out by the use of a hot-press machine, a vacuum hot-press machine, or a hot roll press. Alternatively, a press machine, a vacuum press machine or a roll press, each having a separate heating means installed substantially adjacent thereto, can be used.

[0051] The single-sided metal-foil laminate of the present invention can be used not only as a material for circuit substrates, but also in a variety of applications in which laminates of general-purpose plastics with metal foils are employed. However, particularly where the single-sided metal-foil laminate of the present invention is used as a material for circuit substrates, it is desirable that the physical property such as the thermal expansion coefficient of the liquid crystal polymer film in a film forming direction is equal to or substantially equal to that in a direction perpendicular to the film forming direction. Considering, however, that the liquid crystal polymer molecules tend to be easily oriented, formation of the liquid crystal polymer film with the standard film forming method would result in that the liquid crystal polymer forming the film will have its molecules strongly oriented (with SOR not smaller than 1.5) in the film forming direction. Where the liquid crystal polymer film having the molecules strongly oriented in the film forming direction is used as a material for the single-sided metal-polymer laminate, the liquid crystal polymer layer in the resultant single-sided metal-polymer laminate will have its molecules strongly oriented in the film forming direction as is the case with the raw material film and, therefore, the physical property such as the thermal expansion coefficient in the film forming direction will become different from that in the direction perpendicular to the film forming direction.

[0052] In view of the foregoing, the single-sided metal-polymer laminate for use as a material for the circuit substrates is preferably of a nature in which the liquid crystal polymer film used therein has an isotropy (with SOR not greater than 1.3, and ideally 1).

[0053] As hereinbefore discussed, the present invention is intended to provide the laminate comprising the electric insulating layer made of the liquid crystal polymer and the metallic foil layer, wherein the liquid crystal polymer layer can be made thin, and, in particular, to provide as a suitable material for the circuit substrates the laminate in which the electric insulating layer made of the liquid crystal polymer has an isotropic molecular orientation. Accordingly, the liquid crystal polymer layer used in the single-sided metal-polymer laminate of the present invention makes it possible to provide the circuit substrate comprising the thin liquid crystal polymer layer and the metal foil layer, which substrate has long been desired for, because of the feature of the thin thickness secured and because of the isotropic molecule orientation.

[0054] In any event, the present invention will become more clearly understood from the following description of preferred embodiments thereof, when taken in conjunction with the accompanying drawings. However, the embodiments and the drawings are given only for the purpose of illustration and explanation, and are not to be taken as limiting the scope of the present invention in any way whatsoever, which scope is to be determined by the appended claims. In the accompanying drawings, like reference numerals are used to denote like parts throughout the several views, and:

Figs. 1a to 1c schematically illustrate the sequence of forming a coating on a base material with the use of an isotropic liquid crystal polymer film, showing a coating method according to a first preferred embodiment of the present invention;

Figs. 2a to 2g schematically illustrate the sequence of formation of a single-sided metal-polymer laminate, showing a laminate forming method according to a second preferred embodiment of the present invention; Fig. 3 is a schematic front elevational view showing an apparatus for making the single-sided metal-polymer laminate according to the present invention;

Fig. 4 is a schematic side view of a parts-mounted circuit board according to a third preferred embodiment of the present invention;

Fig. 5 is a schematic side sectional view of a multi-layered circuit board according to a fourth preferred embodiment of the present invention; and

Fig. 6 is a schematic side view showing a measuring apparatus for measuring the segment orientation ratio.

[0055] A method of forming a coating on a base material according to a first preferred embodiment of the present invention is shown in Figs. 1a to 1c. As shown in Fig. 1a, a sheet-like coated material 1 comprises a liquid crystal polymer film 2 thermally bonded to a sheet-like base material 3. The liquid crystal polymer film 2 has a segment orientation ratio (SOR) not greater than 1.3 and has a thickness not smaller than 15  $\mu$ m. The liquid crystal polymer film 2 is subsequently peeled off substantially as shown in Fig. 1b.

Because of the advantageous utilization of the intra-layer separability of the liquid crystal polymer film 2, the peel-off process can be effected easily. The peeling of the liquid crystal polymer film 2 results in separation of the liquid crystal polymer film 2 into two thin liquid crystal polymer plies 2a and 2b with the liquid crystal polymer ply 2a left firmly bonded to the base material 3 while the ply 2b is being peeled off. After the liquid crystal polymer ply 2b has completely been peeled off, the liquid crystal polymer ply 2a remains bonded finally to the base material 3 to thereby form the coated material 1 as shown in Fig. 3c.

[0056] In this way, the coated material 1 including a liquid crystal polymer coating having the SOR not greater than 1.3 and a thickness not greater than 15  $\mu\text{m}$  can easily be obtained owing to the advantageous utilization of the intra-layer separability of the liquid crystal polymer film.

[0057] A method of making the single-sided metal-polymer laminate according to a second preferred embodiment of the present invention is shown in Figs. 2a to 2g. A double-sided metal-polymer laminate 11 comprising the liquid crystal polymer film 2 having its opposite surfaces thermally bonded with upper and lower metal foil layers 3 as shown in Fig. 2a is divided, as shown in Fig. 2b, along a plane intermediate of the thickness of the double-sided metal-polymer laminate 11 so as to separate the liquid crystal polymer film 2 in a thicknesswise direction indicated by Z to provide first and second single-sided metal-polymer laminates 11a and 11b, as shown in Fig. 2c, each comprising a divided liquid crystal polymer layer 2 and the upper or lower metal foil layer 3.

[0058] The process of division shown in Fig. 2b is carried out by the utilization of the intra-layer separability of the liquid crystal polymer film as is the case with the foregoing embodiment and can therefore be easily carried out. The method so far described with reference to Figs. 2a to 2c does not require the use of the expensive release film hitherto required in the practice of the prior art method and is effective to provide the two single-sided metal-polymer laminates simultaneously.

[0059] Either of the resultant single-sided metal-polymer laminates, for example, the single-sided metal-polymer laminate 11b, may further be provided with a similar or different metal foil 3a hot-pressed to one of opposite surfaces of the liquid crystal polymer film layer 2 remote from the lower metal foil layer 3 as shown in Fig. 2d to provide the double-sided metal-polymer laminate 11c as shown in Fig. 2e. However, the double-sided metal-polymer laminate 11c so obtained comprises the liquid crystal polymer layer 2 of a thickness substantially half the thickness thereof in the starting double-side metal-polymer laminate 11 shown in Fig. 2a.

[0060] The double-sided metal-polymer laminate 11c is subsequently subjected to the peel-off process as shown in Fig. 2f to separate the liquid crystal polymer layer 2 along a plane intermediate of the thickness thereof in the thicknesswise direction Z to provide first and second single-sided metal-polymer laminates 11d and 11e, as shown in Fig. 2g, each comprising a divided liquid crystal polymer layer 2 and the upper or lower metal foil layer 3a or 3. By repeating the process of method steps shown in Figs. 2d to 2g, it will readily be understood that the thickness of the liquid crystal polymer layer 2 can further be reduced.

[0061] Fig. 3 schematically illustrates an apparatus for making the single-sided metal-polymer laminate according to the present invention described above. Referring now to Fig. 3, the upper metal foil 3, the liquid crystal polymer film 2 and the lower metal foil 3, all of which are a raw material for any one of the single-sided metal-polymer laminates 11a and 11b, are overlapped with the liquid crystal polymer film 2 intervening between the upper and lower metal foils 3, 3 to thereby provide a sandwich structure. This sandwich structure is subsequently passed through a preheating chamber 20 at which the upper and lower metal foils 3, 3 and the liquid crystal polymer film 2 are preheated to the same temperature. The preheated sandwich structure is then passed through a nipping region between heated rollers 21, 21, which form a hot press, so that the upper and lower metal foils 3, 3 with the liquid crystal polymer film 2 intervening therebetween can be hot-pressed together to thereby provide the double-sided metal-polymer laminate 11. The resultant double-sided metal-polymer laminate 11 is thereafter passed through a temperature-controlled chamber 22 for adjusting the temperature of the double-sided metal-polymer laminate 11 to a value suitable for eventual separation of the double-sided metal-polymer laminate 11 into two single-sided metal-polymer laminates as will be described later.

[0062] The temperature-adjusted double-sided metal-polymer laminate 11 emerging outwardly from the temperature-controlled chamber 22 is then supplied to a separating device 23 by which the double-sided metal-polymer laminate 11 is divided along a plane intermediate of the thickness of the liquid crystal polymer layer 2 to thereby provide the first and second single-sided metal-polymer laminates 11a and 11b which are subsequently wound around respective take-up rolls.

[0063] The third preferred embodiment of the present invention is directed to a parts-mounted circuit board 12 which is conceptually shown in Fig. 4. Referring to Fig. 4, this parts-mounted circuit board 12 is prepared from the single-sided metal-polymer laminate 11a or 11b which is shown in Fig. 2c and in which the metal foil 3 is made of copper, and has an electric circuit formed thereon by etching off a portion of the copper foil 3 in the parts-mounted circuit board 12 other than an area having one or more printed patterns of electric circuits. Electronic component parts 13 such as resistors, coils, capacitors and IC components are surface-mounted on the circuit board 12 and electrically connected with the circuit patterns. Since the present invention makes it possible to reduce the thickness of the liquid crystal polymer layer 2 which serves as an electric insulating layer, the single-sided metal-polymer laminate 11a is effective to provide the parts-mounted circuit board 12 of a reduced thickness.

[0064] The multi-layered circuit substrate 14 according to the fourth preferred embodiment of the present invention will now be described with reference to Fig. 5. As shown schematically therein, the multi-layered circuit substrate 14 comprises a liquid crystal polymer film 4 firmly sandwiched between two double-sided metal-polymer laminates 11c of the structure shown in Fig. 2e. The metal foils 3 employed in each of the double-sided metal-polymer laminates 11c is made of copper. Each of those double-sided metal-polymer laminates 11c has an electric circuit formed thereon by etching off a portion of the respective copper foil 3 other than an area having one or more printed patterns of electric circuits. After the liquid crystal polymer film 4 has been sandwiched between these double-sided metal-polymer laminates 11c, the resultant sandwich structure is hot-pressed to provide the multi-layered circuit substrate 14 which is subsequently



perforated across the thickness thereof to have a plurality of through-holes. An internal wall surface of each of said through-holes are finally plated at 5 to complete the plated through-holes 6 for receiving terminal elements of electronic component parts. Since the present invention makes it possible to reduce the thickness of the liquid crystal polymer layer 2 which serves as an electric insulating layer, the double-sided metal-polymer laminates 11c are effective to provide the multi-layered circuit substrate 14 of a reduced thickness.

[0065] Hereinafter, the present invention will be demonstrated by way of some examples which are set forth only for illustrative purpose and are not for limiting the scope of the present invention.

#### Example I:

[0066] A thermotropic liquid crystal polyester containing 27 mol % of units from 6-hydroxy-2-naphthoic acid and 73 mol % of units from p-hydroxybenzoic acid was heat-kneaded through a single-screw extruder at a temperature of 280 to 300 DEG C and was then extruded through an inflation die, 40 mm in diameter and 0.6 mm in slit size, to produce a liquid crystal polymer film having a thickness of 75  $\mu$ m. The resultant liquid crystal polymer film had a melting point of 280 DEG C and a segment orientation ratio (SOR) of 1.2. An aluminum foil (the base material to be coated) having a thickness of 200  $\mu$ m and the resultant liquid crystal polymer film were, after having been overlapped one above the other, heat-pressed between upper and lower heated plates of a vacuum flat-bed hot press, evacuated to 40 mmHg, at a temperature of 275 DEG C under a pressure of 20 Kg/cm<sup>2</sup>, followed by separation that was carried out so as to allow a portion of the liquid crystal polymer film to be left on the aluminum foil.

[0067] Thereafter, the aluminum foil is etched off by the use of a chemical etching technique to give a liquid crystal polymer coating layer. Measurement of the resultant liquid crystal polymer coating layer has shown that it has a segment orientation ratio of 1.2 and a thickness of 30  $\mu$ m.

[0068] For comparison purpose, the above described liquid crystal polymer was melted and coated on the same aluminum foil (the base material) by the use of a roll coater to provide a liquid crystal polymer coating layer. When this liquid crystal polymer coating layer was measured in the manner described above, the segment orientation ratio was 1.5.

#### Example II

[0069] A thermotropic liquid crystal polyester containing 27 mol % of units from 6-hydroxy-2-naphthoic acid and 73 mol % of units from p-hydroxybenzoic acid was heat-kneaded through a single-screw extruder at a temperature of 280 to 300 DEG C and was then extruded through an inflation die, 40 mm in diameter and 0.6 mm in slit size, to produce a liquid crystal polymer film having a thickness of 20  $\mu$ m. The resultant liquid crystal polymer film had a melting point of 280 DEG C and a segment orientation ratio (SOR) of 1.03.

[0070] The resultant liquid crystal polymer film as a material for the liquid crystal polymer coating layer and an electrolytic copper foil (the base material to be coated) having a thickness of 18  $\mu$ m were, after having been overlapped one above the other, heat-pressed with the use of a vacuum flat-bed hot press in a manner similar to that in Example I and is then separated so as to allow a portion of the liquid crystal polymer film to be left on the copper foil, thereby to provide the liquid crystal polymer coating layer. After the electrolytic copper foil has been etched off by the use of the chemical etching technique, the liquid crystal polymer coating layer was measured, resulting in the segment orientation ratio of 1.03 and the thickness of 9  $\mu$ m. Example III

[0071] A thermotropic liquid crystal polyester containing 27 mol % of units from 6-hydroxy-2-naphthoic acid and 73 mol % of units from p-hydroxybenzoic acid was heat-kneaded through a single-screw extruder at a temperature of 280 to 300 DEG C and was then extruded through an inflation die, 40 mm in diameter and 0.6 mm in slit size, to produce a liquid crystal polymer film having a thickness of 50  $\mu$ m. The resultant liquid crystal polymer film had a melting point of 280 DEG C, a segment orientation ratio (SOR) of 1.02 and a thermal expansion coefficient of -8 ppm/ DEG C.

[0072] The resultant liquid crystal polymer film as a material for the liquid crystal polymer coating layer and a rolled copper foil having a thickness of 10  $\mu$ m and a thermal expansion coefficient of 18 ppm/ DEG C, were, after having been overlapped one above the other, heat-pressed with the use of a vacuum flat-bed hot press in a manner similar to that in Example I and is then separated so as to allow a portion of the liquid crystal polymer film to be left on the copper foil, thereby to provide the liquid crystal polymer coating layer. After the rolled copper foil has been etched off by the use of the chemical etching technique, the liquid crystal polymer coating layer was measured, resulting in the segment orientation ratio of 1.02 and the thickness of 15  $\mu$ m. The thermal expansion coefficient was found -8 ppm/ DEG C.

#### Example IV

[0073] The base material having the liquid crystal polymer coating layer obtained in Example III was heated to 292 DEG C with the use of an oven of a hot-air circulating type. The rolled copper foil was etched off by the use of the chemical etching technique. The resultant liquid crystal polymer coating layer has shown a segment orientation ratio of 1.02, a thickness of 15  $\mu$ m and a thermal expansion coefficient of 18 ppm/ DEG C.

#### Example V

[0074] The same liquid crystal polymer film as that in Example III above, having the same thickness of 50  $\mu\text{m}$  as that in Example III, was sandwiched between an electrolytic copper foil of 18  $\mu\text{m}$  in thickness as an upper metal foil and an electrolytic copper foil of 18  $\mu\text{m}$  in thickness as a lower metal foil and was heat-pressed by a vacuum flat-bed hot press, evacuated to 30 mmHg, at a press temperature of 270 DEG C under a pressure of 60 Kg/cm<sup>2</sup>, to produce a double-sided metal-polymer laminate having a thickness of 86  $\mu\text{m}$ . The liquid crystal polymer film used had a segment orientation ratio of 1.02.

[0075] The resultant double-sided metal-polymer laminate was separated along a plane intermediate of the thickness thereof to provide two single-sided metal-polymer laminates. The liquid crystal polymer layer in each of those single-sided metal-polymer laminates showed a surface of separation which is smooth flat and free from fluffs. Each of the resultant single-sided metal-polymer laminates had a thickness of 43  $\mu\text{m}$  and, since the single metal foil used had a thickness of 18  $\mu\text{m}$ , the thickness of the liquid crystal polymer layer in each of the single-sided metal-polymer laminates was 25  $\mu\text{m}$ , accordingly.

[0076] The metal foil in each of the single-sided metal-polymer laminate was then etched off by the use of the chemical etching technique to leave a film-like liquid crystal polymer layer which was found having a segment orientation ratio of 1.02, with no variation having consequently occurred in the segment orientation ratio.

#### Example VI

[0077] By applying a force to upper and lower portions of the same double-sided metal-polymer laminate of 86  $\mu\text{m}$  in thickness as that in Example V, which are adjacent the upper and lower metal foils, respectively, so as to separate the liquid crystal polymer layer upwardly and downwardly at a position different from Example V, a first laminate including the upper metal foil layer and a divided liquid crystal polymer layer and a second laminate including the lower metal foil and a divided liquid crystal polymer layer were prepared.

[0078] The first laminate had a thickness of 48  $\mu\text{m}$  and, hence, the liquid crystal polymer layer of the first laminate had a thickness of 30  $\mu\text{m}$  whereas the second laminate had a thickness of 38  $\mu\text{m}$  and, hence, the liquid crystal polymer layer of the second laminate had a thickness of 20  $\mu\text{m}$ .

[0079] The respective metal foil layers of the first and second laminates were subsequently etched off by the use of the chemical etching technique. Both of the resultant liquid crystal polymer layers in the first and second laminates had a segment orientation ratio of 1.02. Example VII

[0080] A thermotropic liquid crystal polyester containing 27 mol % of units from 6-hydroxy-2-naphthoic acid and 73 mol % of units from p-hydroxybenzoic acid was heat-kneaded through a single-screw extruder at a temperature of 280 to 300 DEG C and was then extruded through an inflation die, 40 mm in diameter and 0.6 mm in slit size, to produce a liquid crystal polymer film having a thickness of 16  $\mu\text{m}$ . The resultant liquid crystal polymer film had a melting point of 280 DEG C and a segment orientation ratio (SOR) of 1.02.

[0081] The resultant liquid crystal polymer film of 16  $\mu\text{m}$  in thickness was sandwiched between two electrolytic copper foils each having a thickness of 18  $\mu\text{m}$  and then thermally bonded together with the use of a pair of hot press rolls heated to a roll temperature of 280 DEG C with a line pressure of 100 kg/cm to thereby provide a double-sided metal-polymer laminate comprising the upper and lower metal foil layers with the liquid crystal polymer layer sandwiched therebetween. This double-sided metal-polymer laminate had a thickness of 52  $\mu\text{m}$ .

[0082] Thereafter, upper-side and lower-side portions of the double-sided metal-polymer laminate were separated in a manner that they were peeled away from each other by the application of a force thereto, to divide the liquid crystal polymer layer into upper and lower polymer layers, to thereby provide a first laminate including the upper metal foil layer and the upper liquid crystal polymer layer and a second laminate including the lower metal foil layer and the lower liquid crystal polymer layer.

[0083] The first laminate had a thickness of 26  $\mu\text{m}$  and, hence, the liquid crystal polymer layer in the first laminate had a thickness of 8  $\mu\text{m}$  whereas the second laminate had a thickness of 26  $\mu\text{m}$  and, hence, the liquid crystal polymer layer in the second laminate had a thickness of 8  $\mu\text{m}$ , as well.

[0084] The respective metal foil layers of the first and second laminates were subsequently etched off by the use of the chemical etching technique. Both of the resultant liquid polymer layers in the first and second laminates had a segment orientation ratio of 1.02. Example VIII

[0085] An electrolytic copper foil having a thickness of 18  $\mu\text{m}$  is placed on the liquid crystal polymer layer of the laminate of 26  $\mu\text{m}$  in thickness obtained in Example VII and is then heat-bonded thereto in a manner similar to that in Example VII to provide a laminate comprising the upper metal foil layer and a lower metal foil layer with the liquid crystal polymer layer sandwiched therebetween. This resultant laminate had a thickness of 44  $\mu\text{m}$ .

[0086] Thereafter, upper-side and lower-side portions of the laminate of 44  $\mu\text{m}$  were separated in a manner that they were peeled away from each other by the application of a force thereto, to divide the liquid crystal polymer layer into upper and lower polymer layers, to thereby provide a first laminate including the upper metal foil layer and the upper liquid crystal polymer layer and a second laminate including the lower metal foil layer and the lower liquid crystal polymer layer.

[0087] The first laminate had a thickness of 22  $\mu\text{m}$  and, hence, the liquid crystal polymer layer in the first laminate had a thickness of 4  $\mu\text{m}$  whereas the second laminate had a thickness of 22  $\mu\text{m}$  and, hence, the liquid crystal polymer layer in the second laminate had a thickness of 4  $\mu\text{m}$ , as well.

[0088] The respective metal foil layers of the first and second laminates were subsequently etched off by the use of the chemical etching technique. Both of the resultant liquid polymer layers in the first and second laminates had a segment orientation ratio of 1.02.

#### Example IX

[0089] An electrolytic copper foil having a thickness of 18  $\mu\text{m}$  is placed on the liquid crystal polymer layer of the laminate of 22  $\mu\text{m}$  in thickness obtained in Example VIII and is then heat-bonded thereto by the use of a hot press heated to a press temperature of 294 DEG C under a pressure of 20  $\text{kg}/\text{cm}^2$  to provide a laminate comprising the upper metal foil layer and a lower metal foil layer with the liquid crystal polymer layer sandwiched therebetween. This resultant laminate had a thickness of 40  $\mu\text{m}$ . Thereafter, the metal foil layers in this laminate were subsequently etched off to define a circuit within an area of 15 x 15 mm, which circuit is thermally fitted to a semiconductor chip to thereby complete a parts-mounted circuit board.

#### Example X

[0090] An electrolytic copper foil having a thickness of 18  $\mu\text{m}$  is placed on the liquid crystal polymer layer of the laminate of 22  $\mu\text{m}$  in thickness obtained in Example VIII and is then heat-bonded thereto by the use of a hot press heated to a press temperature of 294 DEG C under a pressure of 20  $\text{kg}/\text{cm}^2$  to provide two laminates each comprising the upper metal foil layer and a lower metal foil layer with the liquid crystal polymer layer sandwiched therebetween. Each of the resultant laminates had a thickness of 40  $\mu\text{m}$ . Thereafter, a circuit pattern was formed by the use of an etching technique on the metal foil in each of the resultant laminates of 40  $\mu\text{m}$  in thickness. The same liquid crystal polymer film of 50  $\mu\text{m}$  in thickness as that used in Example III was sandwiched between the two laminates having the respective circuit patterns formed thereon and was then heat-bonded together by the use of a hot press heated to a press temperature of 284 DEG C under a pressure of 10  $\text{kg}/\text{cm}^2$  to provide a single laminate of a multi-layered structure. Then, portions of the circuit patterns which eventually serve as terminal connections were drilled to form through-holes which were subsequently copper-plated by means of a crimson non-electrolytic plating method to thereby complete a multi-layered circuit substrate.

[0091] As hereinbefore fully described, the present invention is effective to provide a means for forming the isotropic liquid crystal polymer coating layer and, in particular, a means for forming the isotropic liquid crystal polymer coating layer having a thickness not greater than 15  $\mu\text{m}$  and the isotropic liquid crystal polymer coating layer having a thermal expansion coefficient that is equal to or substantially equal to that of the base material.

[0092] Also, according to the present invention, the single-sided metal-polymer laminate utilizing the liquid crystal polymer can be manufactured with no need to use any release film hitherto required. For this reason, the cost hitherto incurred by the use of the release film can be eliminated. Also, since two single-sided metal-polymer laminates can be manufactured from the single double-sided metal-polymer laminate through a single process, the single-sided metal-polymer laminates according to the present invention can be produced at a speed substantially twice that required according to the prior art method, accompanied by increase in productivity.

[0093] In addition, as hereinbefore fully described, the present invention is effective to provide the laminate comprising the ultra-thin liquid crystal polymer layer and the metal foil layer and the laminate containing the liquid crystal polymer layer having a segment orientation ratio that is uniform in any direction in a plane.

[0094] Although the present invention has been fully described in connection with the preferred embodiments thereof with reference to the accompanying drawings which are used only for the purpose of illustration, those skilled in the art will readily conceive numerous changes and modifications within the framework of obviousness upon the reading of the specification herein presented of the present invention. Accordingly, such changes and modifications are, unless they depart from the scope of the present invention as delivered from the claims annexed hereto, to be construed as included therein.

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## Coating method utilizing a polymer film and method of making metal-polymer laminates

Claims of correspondent: EP0949067

[Translate this text](#)

1. A coating method which comprises the steps of:

applying to a base material a polymer film prepared from a polymer capable of forming an optically anisotropic melt phase and having a segment orientation ratio of not greater than 1.3;  
heat-bonding the polymer film to the base material to provide a laminate; and  
peeling the film so as to leave a thin layer of the film on the base material.

2. A coated material comprising a base material and a coating layer left thereon, which is obtainable by the coating method as defined in Claim 1

3. The coated material as claimed in Claim 2, wherein the coating layer has a thickness not greater than 15  $\mu\text{m}$ .

4. A coated material which comprises a base material and a coating layer made of a polymer capable of forming an optically anisotropic melt phase and having a thickness not greater than 15  $\mu\text{m}$  for coating the base material, wherein the coating layer has a segment orientation ratio of not greater than 1.3.

5. The coated material as claimed in Claims 2, 3 or 4, wherein the coating layer has a thermal expansion coefficient which is substantially equal to that of the base material.

6. A method of making a single-sided metal-polymer laminate which comprises the steps of:

preparing a double-sided metal-polymer laminate including first and second metal foil layer and a layer of a polymer capable of forming an optically anisotropic melt phase, said polymer layer being sandwiched between the first and second metal foil layers; and  
dividing the double-sided metal-polymer laminate so as to separate the polymer layer in a thicknesswise direction to provide a first single-sided metal-polymer laminate including the first metal foil and a layer of the polymer capable of forming an optically anisotropic melt phase and a second single-sided metal-polymer laminate including the second metal foil and a layer of the polymer capable of forming an optically anisotropic melt phase.

7. The method of making the single-sided metal-polymer laminate as claimed in Claim 6, wherein said preparing step is carried out by sandwiching a film of the polymer capable of forming an optically anisotropic melt phase between the first and second metal foils in a layered fashion and hot-pressing them together.

8. A single-sided metal-polymer laminate obtainable by the method as defined in Claim 6 or 7.

9. The single-sided metal-polymer laminate as claimed in Claim 8, wherein the layer of the polymer contained in the single-sided metal-polymer laminate and capable of forming the optically anisotropic melt phase has a thickness not greater than 15  $\mu\text{m}$ .

10. The single-sided metal-polymer laminate as claimed in Claim 8, wherein the layer of the polymer contained in the single-sided metal-polymer laminate and capable of forming the optically anisotropic melt phase has a segment orientation ratio of not greater than 1.3.

11. A single-sided metal-polymer laminate which comprises a layer of a polymer capable of forming an optically anisotropic melt phase and having a thickness not greater than 15  $\mu\text{m}$  and a metal foil layer bonded to one of opposite surfaces of the polymer layer, said layer of the polymer having a segment orientation ratio of not greater than 1.3.

12. A parts-mounted circuit board which comprises a single-sided metal-polymer laminate as defined in any one of Claims 8 to 11, and at least one electronic component part mounted on the single-sided metal-polymer laminate.

13. A multi-layered parts-mounted circuit board which comprises a multi-layered laminate including a single-sided metal-polymer laminate as defined in any one of Claims 8 to 11, said single-sided metal-polymer laminate being overlapped with at least one laminate which is the same as or different from said single-sided metal-polymer laminate, and at least one electronic component part mounted on the multi-layered laminate.

14. A method of making a double-sided metal-polymer laminate, which method comprises the steps of:

applying a metal foil to the polymer layer of the single-sided metal-polymer laminate as defined in any one of Claims 8 to 11; and  
hot pressing the metal foil and the single-sided metal-polymer laminate together to provide the double-sided metal-polymer laminate.

15. A double-sided metal-polymer laminate obtainable by the method as defined in Claim 14.

16. An apparatus for making a single-sided metal-polymer laminate, said apparatus comprising:

a hot press device for hot-pressing a film in a direction across a thickness thereof to provide a double-sided metal-polymer laminate, said film being made of a polymer capable of forming an optically anisotropic melt phase and being sandwiched between first and second metal foils; and  
a separating device for dividing the double-sided metal-polymer laminate so as to separate the polymer layer in a thicknesswise direction to provide a first single-sided metal-polymer laminates including the first metal foil and a layer of the polymer capable of forming an optically anisotropic melt phase and a second single-sided metal-polymer laminate including the second metal foil and a layer of the polymer capable of forming an optically anisotropic melt phase.

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發 明 專 利 說 明 書		
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	英 文	COATING METHOD UTILIZING A POLYMER FILM AND METHOD OF MAKING METAL-POLYMER LAMINATES
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## 四、中文發明摘要（發明之名稱：

使用聚合物薄膜塗層法和聚合物層  
與金屬箔層疊體的製法

本發明提供了一種可以消除各向異性，即提高各向同性的，形成能構成光學各向異性熔融相的聚合物塗層的方法，特別是形成厚度較薄的塗層的方法。在將由可以形成光學各向異性熔融相的聚合物製成的，分子定向度在1.3以下的薄膜2，與被塗層體3熱壓黏接後，剝離薄膜2b，在被塗層體3上殘留前述薄膜2的薄層2a。

英文發明摘要（發明之名稱：COATING METHOD UTILIZING A POLYMER  
FILM AND METHOD OF MAKING METAL-POLYMER  
LAMINATES

A coating layer of a polymer capable of forming an optically anisotropic melt phase is formed by heat-pressing to a base material a film made of the polymer and having a segment orientation ratio of not greater than 1.3 and then separating the film into two halves so as to leave one of the halves on the base material, thereby obtaining a coated material made of the base material and the thin coating layer.



## 五、發明說明(1)

### 技術領域

本發明涉及一種塗層體及其製造方法，該塗層體具有各向同性的塗層，該塗層是將壓接在金屬箔等基體上，由可以形成光學各向異性的熔融相聚合物（以下稱為“液晶聚合物”）製成的薄膜（以下稱為“液晶聚合物薄膜”）的一部分剝離而得到的。本發明還涉及一種液晶聚合物和金屬箔的層疊體，及其製造方法；該層疊體是將壓接在金屬箔上的液晶聚合物薄膜的一部分，沿著層厚的方向撕開而得到的。這裡，所謂塗層體是指，將液晶聚合物塗在被塗層體上，形成液晶聚合物塗層的物體。

### 習知技術

液晶聚合物是：（1）可以與金屬箔直接熱壓接；（2）具有高的耐熱性；（3）低的吸濕性；（4）熱尺寸穩定性好；（5）濕度尺寸穩定性好；（6）高頻特性好；（7）具有沒有添加含有有毒的鹵素，磷，鎘等難燃劑的難燃性；（8）耐藥性好；（9）耐放射線性好；（10）可以控制熱膨脹係數；（11）即使在低溫下也柔軟而有彈性；（12）高的氣體阻擋性（氧等氣體的透過率非常低）。

近年來，通過將這種優良的液晶聚合物，很薄地塗在金屬箔、矽平板，或陶瓷平板等被塗層體上，構成用於精密電路基板，多層電路基板，密封材料，包裝容器等材料的的要求特別高漲。另外，還要求有效地利用耐熱性，耐藥性，低吸水性，氣體阻擋性，作為容易腐蝕的金屬等的保護層的塗層。

## 五、發明說明(2)

首先，說明第一個問題。

在物體表面上形成樹脂等薄的皮膜的方法，作為觀裡加工，塗層加工已為眾所周知。一般，二者有下列區別。塗層是在基體上形成連續的皮膜，主要目的是保護其不受污染或腐蝕，達到美觀的裝飾性，它是利用所賦予的非黏著性和低摩擦性的，而觀裡加工是在腐蝕，銹蝕等化學的和物理的嚴格條件下使用的容器（槽），是管的保護用內部壁厚皮膜的形成法，二者在許多方面是類似的，難以區別。一般，將皮膜厚度在0.5mm以上的稱為觀裡，在0.5mm以下的稱為塗層；另一方面，塗層主要是在結構物表面上形成數十微米左右厚度的膜；而觀裡是形成數百微米以上的厚度。不論那一種說法，因為本發明涉及到基體上形成液晶聚合物的非常薄的皮膜

（厚度在25微米以下，主要是在15微米以下）的技術，因此，可以說是涉及塗層的。

作為塗層的性能的重要項目，首先注意的是對溫度變化的耐久性，它是如何適應被塗層體與塗層的熱膨脹係數不同的問題。典型的塗層方法有：（1）傾倒法（浸漬法），（2）流動塗敷機法，（3）帘式塗料器法，（4）滾筒塗色法，（5）電氣黏接法，（6）刷毛塗敷法，（7）噴霧法，（8）氣相塗層法；但在液晶聚合物塗層的情況下，這些現有的塗層法都不適用。理由是，液晶聚合物分子容易在相互同方向上排列，即容易定向。這是由液晶聚合物特有的性質引起的，在將熔融的液晶聚合物形成

## 五、發明說明(4)

分離型薄膜之間，夾入一塊液晶聚合物薄膜，利用熱平板或熱滾子進行熱壓，使液晶聚合物薄膜熔融，在金屬箔和液晶聚合物熱壓黏接之後，剝離除去該分離型薄膜進行製造。

在這種現有技術的製造方法中，在兩面金屬層疊體的情況下，沒有特別的問題；但在單面金屬箔層疊體的情況下，由於必須剝離除去分離型薄膜，則分離型薄膜便浪費了；因此，製造成本相應提高，成為一個重大問題。另外，由於熔融液晶聚合物薄膜，必須在 $300^{\circ}\text{C}$ 左右的高溫下進行，因此，作為分離型薄膜，必須使用耐熱性好的薄膜，必須使用聚四氟乙烯，聚醯亞胺等高價的材料；因此，分離型薄膜的成本高。實際上，液晶聚合物的單面金屬箔層疊體的以商業為基礎的製造非常困難。

另外，近年來，以電子領域為中心，要求減薄電路基板的厚度的要求日益強烈。如上所述，由於液晶聚合物適用於電路基板的電氣絕緣層，因此，強烈要求實現由薄的液晶聚合物層和金屬箔層構成的電路基板。

因此，作為薄的液晶聚合物層，需要液晶聚合物薄膜。普通的製膜，只能製造在一個方向上分子牢固定向的薄膜。然而，在一個方向上分子牢固定向的薄膜，在分子定向的方向上容易撕開；它是熱尺寸變化率在分子定向方向及與其垂直的方向上，顯著不同的薄膜，即是各向異性的薄膜。這種薄膜難以作為電路基板的電氣絕緣層材料使用。然而，如在第一個問題中所述那樣，作為

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## 五、發明說明(5)

電氣絕緣材料的各向同性的液晶聚合物，做成15微米以下的薄的薄膜很困難，特別是膜厚在10微米以下的薄膜，製造非常困難，至今還沒有報告的例子。

### 發明欲解決之問題

為了解決第一個問題，本發明提供了形成一種消除各向異性，即提高各向同性性質的液晶聚合物塗層的方法；特別是提供了一種形成厚度薄的液晶聚合物塗層的方法。

為了解決第二個問題，本發明提供了一種在液晶聚合物的單面金屬箔層疊體製造中，不需要分離型薄膜的單面金屬箔層疊體的製造方法。另外，本發明還提供了一種用消除了各向異性的液晶聚合物電氣絕緣層和金屬箔層構成的層疊體。

### 解決問題之手段

本發明的塗層方法是將由液晶聚合物構成，分子定向度SOR在1.3以下的薄膜，用熱壓黏接的方法，接合在被層疊體上之後，再剝離薄膜，使前述薄膜的薄層殘留在被層疊體上。這樣，可以容易地形成薄的液晶聚合物塗層。

具有殘留在被塗層體上的塗層的本發明的塗層體，具有可以形成光學各向異性的熔融層的聚合物塗層；前述聚合物層的分子定向度在1.3以下。另外，本發明的被塗層體的優選實施例中的前述塗層厚度在15微米以下。因此，本發明的塗層體的塗層可以確保很薄，並且由於是各向同性的，可

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## 五、發明說明(6)

以利用液晶聚合物的上述優越的特點，能夠作為精密電路基板，多層電路基板，密封材料，包裝容器等的材料。

這裡，分子定向度SOR是指賦予構成分子的鏈段的分子定向程度的指標。它與現有的MOR不同，是考慮了物體厚度的值。這個分子定向度SOR是如下這樣算出的。

首先，利用眾所周知的微波分子定向度測定機，例如，第6圖所示的KS系統公司製的微波分子定向度測定機61，測定透過液晶聚合物薄膜的微波的電場強度（微波透過強度）。該測定機61具有產生照射在液晶聚合物薄膜65上的給定波長的微波MW的微波產生裝置63，微波共振導波管64和透過強度檢測裝置68。上述微波共振導波管64的中心處配置有薄膜65；該薄膜表面與微波MW的進行方向垂直。圖中沒有示出的旋轉機構，可將該薄膜65保持在與微波MW進行方向垂直的平面內，可以在R方向旋轉的狀態。同時，通過使透過薄膜65的微波MW，由設在兩端的一對反射鏡67，67反射而產生共振。透過上述薄膜65後的微波透過強度，由透過強度檢測裝置68檢測。上述透過強度檢測裝置68，利用插入在上述微波共振導波管64內的各方給定位置上的檢測元件68a來測定微波的透過強度。

根據這個微波透過強度的測定值，利用下式可以算出n值（稱為屈折率）

$$m = (Z_0 / \Delta Z) \times (1 - \nu_{max} / \nu_0)$$

式中  $Z_0$  -- 裝置常數；

## 五、發明說明(7)

$\Delta z$  -- 被測定物體的厚度；

$\nu_{max}$  -- 改變微波頻率時，使微波透過強度最大的頻率；

$\nu_0$  -- 平均厚度為零時（即沒有物體時），使微波透過強度最大的頻率。

然後，當相對於微波振動方向的物體的上述 R 方向的旋轉角為  $0^\circ$  時，若令微波振動方向（即，物體分子定向最好的方向）與使微波透過強度最小的方向一致時的  $m$  值為  $m_0$ ，旋轉角為  $90^\circ$  時的  $m$  值為  $m_{90}$ ，則利用  $m_0 / m_{90}$ ，可以計算出分子定向度  $SOR$ 。

對於理想的各向同性的薄膜，這個指標  $SOR$  為 1；用通常的 T 形塑模製膜法得到的分子在一個方向牢固定向的液晶聚合物薄膜的  $SOR$  為 1.5 左右。另外，用通常的各向同性充氣製膜法得出的各向同性薄膜的  $SOR$  在 1.3 以下。

另外，液晶聚合物包括半 1 型液晶聚合物，全 1 型液晶聚合物，半 2 型液晶聚合物，全 2 型液晶聚合物（參見，木長純一著：“用於成型和設計的液晶聚合物”西格馬出版社出版）等所有的液晶聚合物。

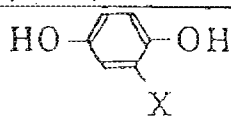
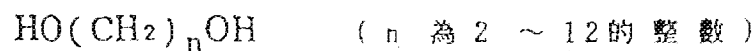
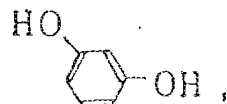
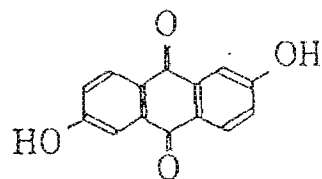
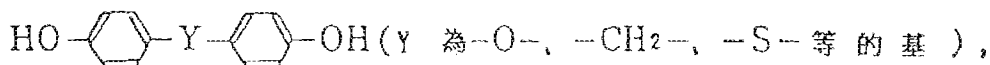
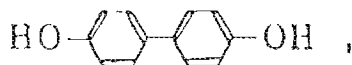
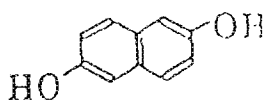
作為液晶聚合物的代表例子，可以舉出以下例示的 (1) 至 (4) 分類的化合物，和由它們的衍生物導出的眾所周知的向熱性液晶聚酯和向熱性的液晶聚酯醯胺。這裡，當然，為了形成高分子液晶，各種原料化合物的組合應有適當的範圍。

## 五、發明說明(8)

(1) 芳香族或脂肪族二羥基化合物 (代表例參見表1)

[表1]

芳香族或脂肪族二羥基化合物的代表例的化學結構式

(X 為氧原子或鹵素原子，  
低級烷基，苯基等基)

(2) 芳香族或脂肪族二羧酸 (代表例參見表2)

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## 五、發明說明(9)

[表 2]

芳香族或脂肪族二羧酸的代表例的化學結構式	
$\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$ ,	$\text{HOOC}-\text{C}_{10}\text{H}_6-\text{COOH}$ ,
$\text{HOOC}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COOH}$ ,	$\text{HOOC}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{COOH}$ ,
$\text{HOOC}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{COOH}$ ,	$\text{HOOC}-\text{C}_6\text{H}_3(\text{COOH})_2$ ,
$\text{HOOC}(\text{CH}_2)_n\text{COOH}$ (n 為 2 ~ 12 的整數)	

## (3) 芳香族羧基羧酸 (代表例參見表 3)

[表 3]

芳香族羧基羧酸的化學結構式	
$\text{HO}-\text{C}_6\text{H}_3(\text{COOH})_2$ X	(X 為 氫 原 子 或 鹵 素 原 子 , 低 級 烷 基 , 苯 基 等 基)
$\text{HO}-\text{C}_{10}\text{H}_6(\text{COOH})_2$ ,	$\text{HO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COOH}$ ,
	$\text{HO}-\text{C}_6\text{H}_3(\text{COOH})_2$

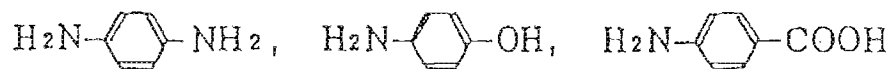
## (4) 芳香族二胺 , 芳香族羧基胺或芳香族胺基酸 (代表例參見表 4)



## 五、發明說明(10)

[表 4]

芳香族二胺，芳香族經基胺或芳香族胺基酸的 代表例的化學結構式
$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2, \quad \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{OH}, \quad \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{COOH}$



(5) 作為由這些原料化合物得出的液晶聚合物的代表例子，可以舉出具有表 5 所示結構單位的共聚體 (a) ~ (e)。

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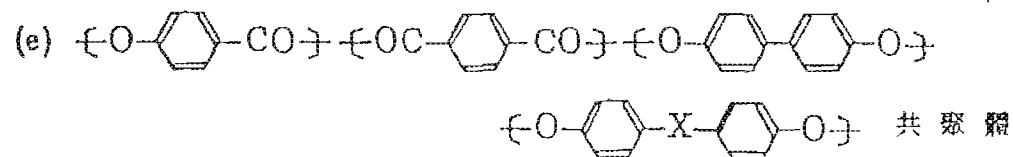
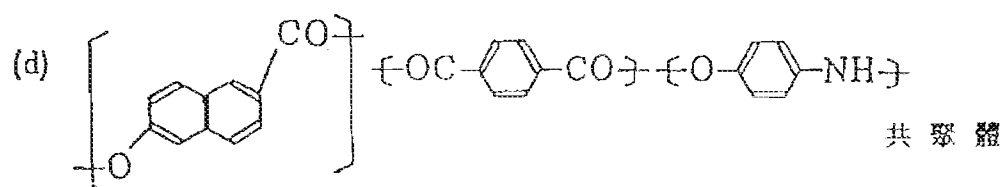
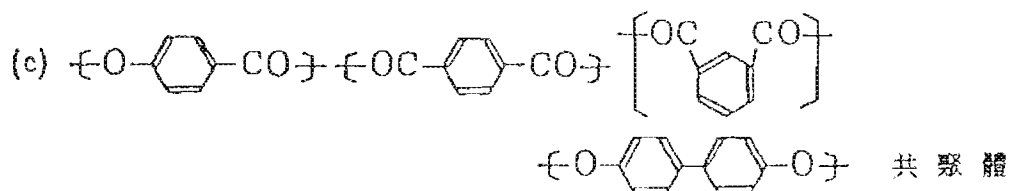
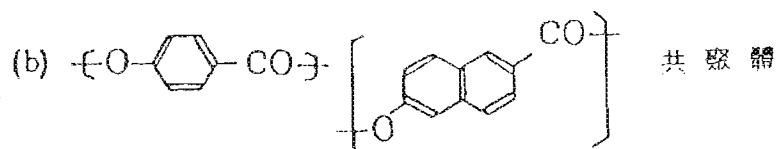
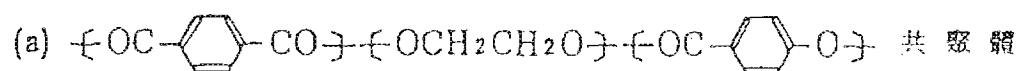
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## 五、發明說明 ( 11 )

[表 5]

液晶聚合物的代表例



(X 為  $-\text{O}-$ ,  $-\text{CH}_2-$ ,  $-\text{S}-$  等的基)

這些液晶聚合物，從薄膜耐熱性和加工性來看，具有向光學各向異性的熔融相轉移的溫度在  $200\sim 400^\circ\text{C}$ ，特別是在  $250\sim 350^\circ\text{C}$  範圍內的液晶聚合物最好。另外，在不損害薄膜的物理性質的範圍內，也可以配合一些潤滑

## 五、發明說明(12)

劑，氧化防止劑，填充材料等。

由上述液晶聚合物製成的薄膜，可以用T塑模法，充氣法，由這些方法組合的方法等眾所周知的製造方法成型。特別是用充氣法，不但可在薄膜的機械軸方向（以下簡稱MD方向），而且可在與它垂直的方向（以下簡稱TD方向）加應力；由於可以得到MD方向或TD方向的機械性質和熱性質平衡的薄膜，因此，能夠較適合地使用。

本發明的重點是利用各向同性的液晶聚合物薄膜作為塗層材料。假如使用分子定向度SOR超過1.3的各向異性的液晶聚合物薄膜作為塗層材料，則在塗層後加熱該薄膜，使各向異性的液晶聚合物塗層熔融，該各向異性塗層也不會轉移至各向同性的液晶聚合物塗層上去。這點是液晶聚合物分子物理性質的基本特性，即使在比液晶聚合物熔點高35℃的溫度下，加熱各向異性的聚合物塗層，也不會變為各向同性，這點已被本發明人確認。

另外，被塗層體的材質為金屬，玻璃，陶瓷等無機物質；塑料，木材，纖維等有機物質。但是，應當使用其軟化點在熱壓黏接液晶聚合物所必要的溫度以上的物質。這裡，作為被塗層體的材質，也包含液晶聚合物本身。例如，加入填充劑或玻璃纖維布等強化材料，或者沒有填充劑或玻璃纖維布，而為了改善被塗層體的表面性質（提高黏接性，力學物理性質，摩擦物理性質，表面潤濕性，氣體阻擋性，耐藥性，耐溶劑性，溶劑親和性，外觀美麗等），在被塗層體的表面上可以設置液晶聚

## 五、發明說明(13)

合物塗層。

特別是，本發明的液晶聚合物塗層，適用於構成電子電路基板的零件，或保持電路基板的零件。在這種情況下，往往是金屬箔就成為被塗層體。作為金屬箔的材質，可以從在電氣連接中使用的金屬等中選擇；最好是金，銀，銅，鎳，鋁，鐵，鋼，錫，黃銅，鎂，鋁，銅／鎳合金，銅／鋁合金，鎳／鉻合金，碳化矽合金，石墨；也可以從它們的混合物構成的群中選擇。

本發明是首先將厚的各向同性液晶聚合物薄膜熱壓黏接在被塗層體上，然後，從被塗層體上剝離該薄膜，將薄的液晶聚合物塗層殘留在該被塗層體上。這點，利用通常的聚合物是難以做到的，但利用液晶聚合物薄膜特有的良好的層內剝離性（在薄膜內部，被剝離成雲母狀的薄層狀的性質），初步有可能成為一種塗層的方法。為了將維持這種良好的層內剝離性各向同性的液晶聚合物薄膜，熱壓黏接在被塗層體上，不需要將加熱溫度提高至液晶聚合物的熔點以上，這是很重要的。

利用這種方法，如果在被塗層體表面上形成的液晶聚合物塗層，加熱至熔點以上，則它可能會失去層內剝離性。另外，將液晶聚合物塗層表面重合在其它物體表面上，在液晶聚合物的熔點以上的溫度下，使被塗層體和其它物體熱壓黏接時，由於在熱壓黏接過程中，液晶聚合物塗層被加熱至熔點以上，因此在液晶聚合物塗層中，不會產生層內剝離。

## 五、發明說明(14)

具有本發明的各向同性的液晶聚合物的塗層體，最好其液晶聚合物塗層的厚度在15微米以下。

液晶聚合物薄膜的製膜技術是很高超的，要製造薄的薄膜很困難，因此製造成本高。通常，由於可以穩定地製造厚度在20微米以上的液晶聚合物薄膜，因此，將液晶聚合物塗層做成20微米以上比較容易。根據情況的不同，也可以不需要上述的剝離過程，而可以形成液晶聚合物塗層。當然，剝離會使剝離面具有微小的粗糙度，作為用黏接劑黏接的表面較好，因此，在大多數情況下，都經過剝離過程，來形成厚度在20微米以上的液晶聚合物塗層，這點是很重要的。特別是在電路基板和其零件的用途中，在要求薄的液晶聚合物塗層的情況下，本發明的塗層體是有效的。為了設置厚度在20微米以下，特別是厚度在15微米以下的各向同性的液晶聚合物塗層，本發明的方法是實用中唯一的方法。能夠實現的液晶聚合物塗層的平均厚度的下限，可以無限地接近零；例如，平均厚度在1微米以下的液晶聚合物塗層可以容易地實現。在精密控制的條件下，也可以實現平均厚度在0.1微米以下的各向同性的液晶聚合物塗層。

具有本發明的各向同性的液晶聚合物塗層的塗層體，最好是各向同性的液晶聚合物塗層的熱膨脹係數，與被塗層體的熱膨脹係數相同。

如先前在“現有技術”一節中所述，希望液晶聚合物塗層的熱膨脹係數，盡可能接近被塗層體的熱膨脹係數。

## 五、發明說明(15)

特別是，對於 $100^{\circ}\text{C}$ 的溫度變化，如果被塗層體和塗層的尺寸變化偏差在 $0.2\%$ 以下，則可以作為電子零件等的精密塗層使用。因而，在這裡，各向同性的液晶聚合物塗層的熱膨脹係數與被塗層體的熱膨脹係數相同，即相對於被塗層體表面的熱膨脹係數，液晶聚合物塗層的熱膨脹係數有正負 $20\text{ppm}/^{\circ}\text{C}$ （即1000件中有正負 $2\%/^{\circ}\text{C}$ ）的偏差。這樣，使被塗層體和塗層的熱膨脹係數接近，最單純的就是使作為塗層原料的液晶聚合物薄膜的熱膨脹係數，與被塗層體的熱膨脹係數相等。即使作為原料的液晶聚合物薄膜的熱膨脹係數，與被塗層體的熱膨脹係數不同，可以通過加熱處理利用該液晶聚合物薄膜製成的液晶聚合物塗層，可以使用兩者的熱膨脹係數相等。在加熱處理時，如果能非常精密地控制加熱溫度，則在測定誤差範圍內，使被塗層體與塗層的熱膨脹係數一致是有可能的。在塗層中使用沒有顯示液晶性的通常的熱可塑性聚合物，或環氧樹脂一類的熱硬化性樹脂的情況下，為了控制熱膨脹係數，則必須進行在塗層中加入無機粉末，或無機編織物，控制它們的比例；或者控制構成塗層的聚合物分子之交聯密度等特別的操作；而在液晶聚合物塗層的情況下，利用液晶聚合物分子的特異的性質，可以只利用加熱處理一類的單純操作就可以實現。

如上所述，本發明的液晶聚合物分子容易定向，由於利用了薄膜狀成型情況下所具有的優良的層內剝離性

## 五、發明說明(16)

，在剝離熱壓黏接在被塗層體表面上的液晶聚合物薄膜過程中，產生層內剝離，再通過使作為原材料的液晶聚合物薄膜厚度方向的一部分，殘留在被塗層體上，可以容易地形成薄的液晶聚合物塗層。

下面要說明本發明的液晶聚合物的金屬箔層疊體的製造方法。在上述液晶聚合物塗層中，被塗層體為金屬箔的情況下，在利用液晶聚合物的層內剝離性來進行製造這一點來看，與本發明的液晶聚合物塗層有關聯性。

本發明的單面金屬箔層疊體的製造方法是通過將兩面金屬箔層疊體，沿前述聚合物層的厚度方向；在上面和下面斷開，分割成由液晶聚合物層及其上面的金屬箔層組成的第一單面金屬箔層疊體，和由液晶聚合物層及下面的金屬箔層組成的第二單面金屬箔層疊體。上述兩面金屬箔層疊體則是由液晶聚合物層、接合在其上表面的金屬箔層和與其下表面接合的金屬箔層構成的。這樣，單面金屬箔層疊體在製造時，可以不需要使用現有的方法中必不可少的分離型薄膜，並且在一次過程中可以製造兩塊單面金屬箔層疊體，因此製造速度大約為原來的兩倍。

利用本發明的單面金屬箔層疊體的製造方法，前述兩面的金屬箔層疊體最好是用兩塊層狀的金屬箔，夾住由液晶聚合物製成的薄膜，然後進行熱壓來製造。

本發明的單面金屬箔層疊體，是利用上述製造方法得到的。

## 五、發明說明(17)

本發明的單面金屬箔層疊體，最好其上述液晶聚合物層厚度在15微米以下。

本發明的單面金屬箔層疊體最好其上述液晶聚合物層的分子定向度在1.3以下。

本發明的安裝電路基板使用上述的單面金屬箔層疊體，將電子零件安放在該層疊體上，並與層疊體連接。

本發明的多層安裝電路基板，則在上述單面金屬箔層疊體上，使用將該層疊體或其它層疊體重合構成的多層層疊體，將電子零件安放在該多層層疊體上，並與該多層層疊體連接。

本發明的兩面金屬箔層疊體的製造方法，是將金屬箔重合在前述單面金屬箔層疊體的前述聚合物層上，進行熱壓，而製造兩面金屬箔層疊體的。

本發明的兩面金屬箔層疊體，是用上述製造方法得到的。

本發明的單面金屬箔層疊體的製造裝置具有一個熱壓裝置和一個分割裝置。該熱壓裝置可以將由兩塊層狀的金屬箔夾緊的液晶聚合物製成的薄膜，沿其厚度方向進行熱壓。該分割裝置可以將由熱壓形成的液晶聚合物層，它上表面上的金屬箔層，和它下表面的金屬箔層構成的兩面金屬箔層疊體，沿著上述聚合物層的厚度方向，斷開成上面和下面的層疊體。

本發明的重點是液晶聚合物層利用由上述的層內剝離性產生的在厚度方向可以分成兩半的性質，來做出以



## 五、發明說明(18)

不喪失這個性質為目的的單面金屬箔層疊體。為此，必須使液晶聚合物層即使軟化，也不熔融；並使液晶聚合物層的溫度不能上升超過熔點。但是，液晶聚合物層的熔點並不是一定的，熔點與加在液晶聚合物層上的熱滯後有關。例如，如果將液晶聚合物薄膜或層放置在熔點附近，但比熔點低的溫度（例如，經常連續的 $15^{\circ}\text{C}$ 的低溫）環境中，熔點隨時間推移而上升，最後，熔點比原來出發時的熔點上升大約 $120^{\circ}\text{C}$ 。這樣，在熔點比出發時升高的時刻，如果溫度不超過那時的熔點，則不會損害液晶聚合物層沿厚度方向分為兩半的性質。

另外，作為熱壓方法可以使用壓力機，真空壓力機，滾筒壓力機等，這些機器實質上是與另外的熱壓機，真空熱壓機，熱滾筒式壓力機和加熱裝置相連接的。

單面金屬箔層疊體不但可用在電路基板上，而且可以用在通用的塑料和金屬箔的層疊體上。另外，特別是在電路基板用途中，希望作為原料的液晶聚合物薄膜的製膜方向，和與它垂直的方向上的熱膨脹係數等物理性質，盡可能相同。但是，液晶聚合物的分子非常容易定向，當利用通常的製膜方法製造液晶聚合物薄膜時，在構成薄膜的液晶聚合物，在製膜方向上，分子定向牢固

（分子定向度 $SOR$ 在大約 $1.5$ 以上）。在以這種在製膜方向上分子牢固定向的液晶聚合物薄膜，作為單面金屬箔層疊體的原料的情況下，單面金屬箔層疊體的液晶聚合物層，在與原料薄膜相同的製膜方向上也是牢固定向

## 五、發明說明(19)

的，因此，在製膜方向和與它垂直的方向上，熱膨脹係數等物理性質不一致。

另外，特別是在電路基板用途中，希望用於單面金屬箔層疊體製造的液晶聚合物薄膜為各向同性的（分子定向度SOR在1.3以下，理想的值希望SOR為1）。

如上所述，本發明提供了由液晶聚合物電氣絕緣層和金屬箔構成的層疊體，另外還提供了液晶聚合物層可以做得很薄，作為電路基板特別希望的，液晶聚合物電氣絕緣層層的分子定向為各向同性的層疊體。因此，由於本發明的單面層疊體的液晶聚合物層在確保可以做得很薄的同時，還具有各向同性性質，因此可以實現在實際中強烈希望的，由薄液晶聚合物層和金屬箔構成的電路基板。

### 圖式簡單說明

第1(a)～1(c)圖表示利用本發明的第一個實施例的各向同性的液晶聚合物薄膜的塗層方法的說明圖；

第2(a)～2(g)圖表示利用本發明的第二個實施例的單面金屬箔層疊體的製造方法的說明圖；

第3圖為本發明的單面金屬箔層疊體的製造裝置的正視圖；

第4圖為表示本發明的第三個實施例的安裝電路基板的概念圖；

第5圖為本發明的第四個實施例的多層安裝電路基板的剖面的概略圖；

第6圖為表示分子定向度測定機的概略結構的側視圖。

## 五、發明說明(20)

### 實施形態說明

第1(a)~1(c)圖表示使用本發明的第一個實施例的各自向同性的液晶聚合物薄膜的塗層方法。如第1(a)圖所示，塗層體1是將液晶聚合物薄膜2，熱壓黏接在被塗層體3上形成的。液晶聚合物薄膜2的分子定向度SOR在1.3以下，厚度在15微米以上。如第1(b)圖所示，薄的液晶聚合物塗層2a殘留在被塗層體3上，其它的液晶聚合物薄膜2b則剝離掉。由於利用了液晶聚合物薄膜的層內剝離性，因此可以容易地剝離該液晶聚合物薄膜2b以後，就構成了在被塗層體3上塗了一層薄的液晶聚合物層2a的塗層體1。

利用這種塗層方法，可以製造分子定向度SOR在1.3以下，液晶聚合物塗層厚度在15微米以下的塗層體。

第2(a)~2(g)圖表示本發明的第二個實施例的單面金屬箔層疊體的製造方法。如第2(b)圖所示，由第2(a)圖所示的液晶聚合物薄膜2，上表面的金屬箔層3和下面的金屬箔層3構成的兩面金屬箔層疊體11，可以在液晶聚合物層2的厚度方向Z上，(例如)在厚度方向的中心，被撕開成上面的層疊體和下面的層疊體。這樣，如第2(c)圖所示，分割成由上表面的金屬箔層3和液晶聚合物層2構成的第一個單面金屬箔層疊體11a；和由下表面金屬箔3與液晶聚合物層2構成的第二個單面金屬箔層疊體11b。

與第一個實施例同樣，由於利用了液晶聚合物薄膜的層內剝離性，因此容易進行第2(b)圖所示的液晶聚合物

## 五、發明說明(21)

層 2 的撕開工序。

利用第 2(a)~2(c)圖的工序，可以不使用分離型薄膜，同時製造兩個液晶聚合物的單面金屬箔層疊體。

又如第 2(d)圖所示，當使金屬箔 3a 與該單面金屬箔層疊體 11b 的液晶聚合物層 2 重合，並熱壓在一起時，可得到第 2(e)圖所示的兩面金屬箔層疊體 11c。然而，與分割前的兩面金屬箔層疊體 11 比較，液晶聚合物層 2 的厚度大約只有一半。另外，如第 2(f)圖所示，當將該兩面金屬箔層疊體 11c，在厚度方向 Z 上撕開成上面的層疊體和下面的層疊體時，則如第 2(g)圖所示，分割成由上表面的金屬箔層 3a 和液晶聚合物層 2 構成的第一個單面金屬箔層疊體 11d；和由下表面金屬箔層 3 與液晶聚合物層 2 構成的第二個單面金屬箔層疊體 11e。反覆進行第 2(d)~2(g)圖的工序，可進一步將液晶聚合物層 2 的厚度做得很薄。

第 3 圖表示本發明的單面金屬箔層疊體的製造設備的一個具體例子。單面金屬箔層疊體的製造方法如下。將作為單面金屬箔層疊體 11a，11b 的原材料的上表面金屬箔 3，液晶聚合物薄膜 2，和下表面的金屬箔 3 重合；在預熱腔 20 中，使金屬箔 3，3 和液晶聚合物薄膜 2 通過同一溫度，然後利用由作為熱壓裝置的熱壓滾子 21，21 進行熱壓，形成液晶聚合物的兩面金屬箔層疊體 11。其次，使該兩面金屬箔層疊體 11 通過溫度調整腔 22，該調整腔用於將層疊體 11 調整至將其分為上面和下面兩

## 五、發明說明 (22)

個層疊體的適當溫度。此後，在分割裝置23中，在厚度方向，將該兩面金屬箔層疊體11分為上面層疊體和下面層疊體；再將單面金屬箔層疊體11a和單面金屬箔層疊體11b卷繞起來。

第4圖為表示本發明的第三個實施例的安裝電路基板的概念圖。安裝電路基板12的、按第二個實施例製造的單面金屬箔層疊體11a（第2(c)圖）的金屬箔3為銅箔，印刷圖形以外的銅箔，用腐蝕的方法除去，就形成了電路圖形。電阻，線圈，電容器和集成電路(IC)等電子元件13安裝在該電路圖形上，並與電路圖形連接。由於可將本發明的單面金屬箔層疊體11a的，作為電氣絕緣層的液晶聚合物層2做得很薄，因此，可以實現厚度很薄的安裝電路基板12。

第5圖表示將液晶聚合物薄膜4夾緊重合在本發明的兩面金屬箔層疊體之間的本發明第四個實施例的多層電路基板14的剖面概略圖。兩面金屬箔層疊體11c（第2(e)圖）的金屬箔3為銅箔，利用腐蝕方法，除去印刷圖形部分以外的銅箔，就可形成電路圖形。在形成了該電路圖形的兩個兩面金屬箔層疊體11c之間，夾著液晶聚合物薄膜4，在熱壓之後，鑽出元件安裝孔，再進行電鍍5，形成通孔6。由於可以將作為電氣絕緣層的液晶聚合物層2做得很薄，因此，本發明的兩面金屬箔層疊體11c可以實現厚度很薄的多層電路基板14。

以下，利用實施例來詳細說明本發明，但本發明不是

## 五、發明說明(23)

僅局限於這些實施例。

## 實施例 1

首先，利用單軸擠壓機，在  $280^{\circ}\text{C} \sim 300^{\circ}\text{C}$  下，加熱混揉 27 莫耳 % 的 6-羥基-2-萘酸，73 莫耳 % 的 p-羥基安息香酸構成的向熱性液晶聚酯；使它們從直徑為 40 mm，狹縫間隔為 0.6 mm 的充氣模型中擠出，得到厚度為 75 微米的液晶聚合物薄膜。所得出的液晶聚合物薄膜的熔點為  $280^{\circ}\text{C}$ ，其分子定向度 SOR 為 1.2。將厚度為 200 微米的鋁箔（被塗層體）和該液晶聚合物薄膜重合起來，利用真空平板熱壓機，從上下兩方全部抽成 40 mmHg 的真空；然後在  $275^{\circ}\text{C}$  的溫度和  $20\text{ kg/cm}^2$  的壓力下，熱壓黏接後，將該層疊體剝離，殘留一部分該液晶聚合物薄膜。

然後，利用化學腐蝕方法除去鋁箔，測定所得到的液晶聚合物塗層的分子定向度 SOR 為 1.2，塗層厚度為 30 微米。

為了比較，將在同一鋁箔（被塗層體）上的上述液晶聚合物熔融，用滾筒塗料法進行塗層，得到液晶聚合物塗層。如上所述那樣，測定液晶聚合物塗層的分子定向度 SOR 為 1.5。

## 實施例 2

利用單軸擠壓機，在  $280^{\circ}\text{C} \sim 300^{\circ}\text{C}$  下，加熱混揉 27 莫耳 % 的 6-羥基-2-萘酸，73 莫耳 % 的 p-羥基安息香酸構成的向熱性液晶聚酯；使它們從直徑為 40 mm，狹縫間隔為 0.6 mm 的充氣模型中擠出，得到厚度為 20 微米的液晶

## 五、發明說明(24)

聚合物薄膜。所得到的液晶聚合物薄膜的熔點為 $280^{\circ}\text{C}$ ，其分子定向度SOR為1.03。

以上述的液晶聚合物薄膜作為液晶聚合物塗層的材料，與厚度為18微米的電解銅箔（被塗層體）重合，利用真空熱壓機，與實施例1同樣熱壓黏接後，進行剝離，殘留一部分該液晶聚合物薄膜，就得到液晶聚合物塗層。再利用化學腐蝕方法，除去電解銅箔，測定液晶聚合物塗層的分子定向度SOR和厚度，分別為1.03和9微米。

實施例3

利用單軸擠壓機，在 $280^{\circ}\text{C} \sim 300^{\circ}\text{C}$ 下，加熱混揉27莫耳%的6-羥基-2-萘酸，73莫耳%的p-羥基安息香酸構成的向熱性液晶聚酯；使它們從直徑為40mm，狹縫間隔為0.6mm的充氣模型中擠出，得到厚度為50微米的液晶聚合物薄膜。所得到的液晶聚合物薄膜的熔點為 $280^{\circ}\text{C}$ ，分子定向度SOR為1.02，熱膨脹係數為 $8\text{ppm}/^{\circ}\text{C}$ 。

以上述的液晶聚合物薄膜作為液晶聚合物塗層材料，以厚度為18微米，熱膨脹係數為 $18\text{ppm}/^{\circ}\text{C}$ 的壓延銅箔作為被塗層體的材料，使兩者重合；再利用真空熱壓機與實施例1同樣，進行熱壓黏接進行剝離，殘留一部分該液晶聚合物薄膜，就得到液晶聚合物塗層。對壓延銅箔進行化學腐蝕，測定所得到的液晶聚合物塗層的分子定向度SOR和厚度，分別為1.02和15微米。熱膨脹係數為 $8\text{ppm}/^{\circ}\text{C}$ 。

實施例4

## 五、發明說明(25)

將實施例3得到的有液晶聚合物塗層的被塗層體，用熱風循環式乾燥箱加熱至292℃。通過化學腐蝕除去壓延銅箔，得到的液晶聚合物塗層的分子定向度SOR為1.2，厚度為15微米，熱膨脹係數為18ppm/℃。

### 實施例5

以厚度為18微米的電解銅箔做上表面的金屬箔，以厚度為18微米的電解銅箔做下表面的金屬箔，在這兩塊金屬箔之間，夾入與實施例3中所用的相同的，厚度為50微米的液晶聚合物薄膜；再利用真空平板熱壓機在30mmHg的真空下和在壓接溫度為270℃，擠壓壓力為60kg/cm<sup>2</sup>下對全體進行熱壓，製成厚度為86微米的兩面金屬箔層疊體。這裡所用的液晶聚合物薄膜的分子定向度SOR為1.02。

將上述兩面金屬箔層疊體，沿其厚度方向，在中心處分離為上面層疊體和下面層疊體，可得到兩塊單面的金屬箔層疊體。液晶聚合物層的分離面是平滑的，沒有毛刺立起。該兩塊單面金屬箔層疊體的厚度均為43微米，扣除金屬箔的厚度18微米，則液晶聚合物層的厚度為25微米。

利用化學腐蝕方法除去這樣得出的單面金屬箔層疊體上的電解銅箔。殘留的薄膜狀的液晶聚合物層的分子定向度SOR為1.02，分子定向度沒有變化。

### 實施例6

在與實施例5不同的另外位置上，對實施例5中製作

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## 五、發明說明 (26)

的厚度為86微米的兩面金屬箔層疊體的上表面金屬箔層，和下表面金屬箔層加力進行剝離，將液晶聚合物層分成上下兩部分；製作出由上端的金屬箔層和液晶聚合物層構成的第一個層疊體，和由下端的金屬箔層與液晶聚合物層構成的第二個層疊體。

第一個層疊體的厚度為48微米，因此其液晶層厚度為30微米；而第二個層疊體的厚度為38微米，因此其液晶聚合物層厚度為20微米。

用化學腐蝕方法除去上述第一個層疊體和第二個層疊體的金屬箔層。所得出的液晶聚合物層的分子定向度SOR，對第一個層疊體和第二個層疊體均為1.02。

## 實施例7

利用單軸擠壓機，在 $280^{\circ}\text{C} \sim 300^{\circ}\text{C}$ 下，加熱混揉27莫耳%的6-羥基-2-萘酸，73莫耳%的p-羥基安息香酸構成的向熱性液晶聚酯；使它們從直徑為40mm，狹縫間隔為0.6mm的充氣模型中擠出，得到厚度為16微米的液晶聚合物薄膜。所得到的液晶聚合物薄膜的熔點為 $280^{\circ}\text{C}$ ，其分子定向度SOR為1.02。

將上述厚度為18微米的液晶聚合物薄膜，夾在厚度為18微米的兩塊電解銅箔之間，然後用一對熱壓滾子在 $280^{\circ}\text{C}$ 的溫度和 $100\text{kg}/\text{cm}^2$ 的線壓力下進行熱黏接，製成由上表面金屬箔層，液晶聚合物層和下表面層疊體層構成的層疊體。實施例層疊體厚度為52微米。

其次，對厚度為52微米的上述層疊體的上表面金屬箔

## 五、發明說明(27)

層，和下表面金屬箔層加力進行剝離，將液晶聚合物層分成上下兩部分；製成由上端的金屬箔層和液晶聚合物層構成的第一個層疊體和由下表面金屬箔層與液晶聚合物層構成的第二個層疊體。

第一個層疊體的厚度為26微米，因此其液晶聚合物層的厚度為8微米；而第二個層疊體的厚度為26微米，因此其液晶聚合物層的厚度也為8微米。

用化學腐蝕方法除去上述第一個層疊體和第二個層疊體的金屬箔層。所得出的液晶聚合物層的分子定向度S<sub>OR</sub>，對第一個層疊體和第二個層疊體均為1.02。

### 實施例8

將厚度為18微米的一塊電解銅箔，重合在實施例7得出的厚度為26微米的塗層體的液晶聚合物層上，與實施例7同樣進行熱黏接，製造由上表面金屬箔層，液晶聚合物層和下表面金屬箔層構成的層疊體。層疊體的厚度為44微米。

其次，對厚度為44微米的上述層疊體的上表面金屬箔層加力進行剝離，將液晶聚合物層分成上下兩部分；製造由上端金屬箔層和液晶聚合物層構成的第一個層疊體，和由下端金屬箔層與液晶聚合物層構成的第二個層疊體。

第一個層疊體的厚度為22微米，因此其液晶聚合物層的厚度為4微米；而第二個層疊體的厚度為22微米，因此其液晶聚合物層的厚度為4微米。

## 五、發明說明(28)

用化學腐蝕方法除去上述第一和第二個層疊體的金屬箔層。所得出的液晶聚合物層的分子定向度SOR，對第一個和第二個層疊體均為1.02。

## 實施例9

將厚度為18微米的一塊電解銅箔重合在實施例8中得出的厚度為22微米的層疊體的液晶聚合物層上，利用熱壓機在294℃溫度和20kg/cm<sup>2</sup>壓力下，進行熱壓黏接，製造由上表面金屬箔層，液晶聚合物層和下表面金屬箔層構成的層疊體。層疊體的厚度為40微米。腐蝕該層疊體的金屬箔層，在15×15mm的四方形範圍內，形成電路，將該電路熱固定貼緊在半導體芯片上，製成安裝電路基板。

## 實施例10

將厚度為18微米的一塊電解銅箔，重合在實施例8中得出的厚度為22微米的層疊體的液晶聚合物層上，利用熱壓機在294℃溫度和20kg/cm<sup>2</sup>壓力下進行熱壓黏接，製造兩塊由上表面金屬箔層，液晶聚合物層和下表面金屬箔層構成的層疊體。層疊體的厚度為40微米。利用腐蝕方法，在這樣做出的兩塊厚度為40微米的層疊體的金屬箔上形成電路圖形。在兩個形成電路圖形的層疊體間，夾著與實施例3所用的相同的，厚度為50微米的液晶聚合物薄膜；然後在284℃的熱壓溫度和10kg/cm<sup>2</sup>的壓力下進行熱壓，做成多個層。然後，在電路圖形中的連接部分的位置上，用鑽頭鑽出通孔之後，利用紫紅色無

## 五、發明說明(29)

電解銅電鍍法，形成電鍍的通孔，製成多層電路基板。

如上所述，本發明提供了形成各向同性的液晶聚合物塗層的方法，特別是還提供了形成厚度在15微米以下的各向同性的液晶聚合物塗層，各向同性的液晶聚合物塗層的熱膨脹係數與被塗層體的熱膨脹係數相同的各向同性的液晶聚合物塗層的方法。

又如上所述，利用本發明的方法，不需要分離型薄膜，即可以製造液晶聚合物的單面金屬箔層疊體。因此，只需要一次過程，就可由一塊兩面金屬箔層疊體製造兩塊單面的金屬箔層疊體；因此，可以用比現有技術的單面金屬箔層疊體製造方法大約兩倍的速度進行生產，可使生產率提高。

又如上所述，本發明提供了由超薄的液晶聚合物層和金屬箔層構成的層疊體，以及該液晶聚合物層的分子定向在平面內的任何方向上都均等的層疊體。

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## 五、發明說明(20)

## 符號說明

- 1.....塗層體
- 2,4.....液晶聚合物薄膜
- 2a.....液晶聚合物薄膜層
- 2b.....其他的液晶聚合物薄膜
- 3.....被塗層體
- 3a.....金屬箔
- 5.....電鍍
- 6.....通孔
- 11,11c.....兩面金屬箔層疊體
- 11a,11d...第一個單面金屬箔層疊體
- 11b,11e...第二個單面金屬箔層疊體
- 12.....安裝電路基板
- 13.....電子元件
- 14.....多層電路基板
- 20.....預熱腔
- 21.....熱壓滾子
- 22.....溫度調整腔
- 23.....分割裝置

(請先閱讀背面之注意事項再填寫本頁)

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## 六、申請專利範圍

第 88105431 號「使用聚合物薄膜塗層法和聚合物層與金屬箔層疊體的製法」專利案

(89 年 9 月 6 日修正)

## 六 申請專利範圍：

1. 一種塗層方法，其特徵為，在將由可以形成光學各向異性的熔融相的聚合物製成的，分子定向度在 1.3 以下的薄膜，熱壓黏接在被塗層體上之後，剝離該薄膜，以在被塗層體上殘留前述薄膜的薄層。
2. 一種塗層體，其特徵為，它具有用如申請專利範圍第 1 項所述的塗層方法得出的殘留在前述被塗層體上的塗層。
3. 如申請專利範圍第 2 項之塗層體，其中塗層的厚度在 15 微米以下。
4. 一種塗層，其特徵為，它具有可以形成厚度在 15 微米以下的光學各向異性的熔融相的聚合物的塗層和被塗層體；前述聚合物層的分子定向度在 1.3 以下。
5. 如申請專利範圍第 2 至 4 項中任一項的塗層體，其中塗層的熱膨脹係數與被塗層體的熱膨脹係數相同。
6. 一種單面金屬箔層疊體之製造方法，其特徵為，將由可以形成光學各向異性的熔融相的聚合物層，其上表面的金屬箔層和下表面的金屬箔層構成的兩面金屬箔層疊體，沿前述聚合物層的厚度方向，撕開為上面的層疊體和下面的層疊體，從而分割成由可以形成光學各向異性的熔融相的聚合物層，和它上表面的金屬箔層構成的第一單面金屬箔層疊體；和由可以形成光學

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## 六、申請專利範圍

各向異性的熔融相的聚合物層，及其下表面的金屬箔層構成的第二單面金屬箔層疊體。

7. 如申請專利範圍第 6 項的單面金屬箔層疊體之製造方法，其中兩面金屬箔層疊體是用兩塊層狀的金屬箔夾住由可以形成光學各向異性的熔融相的聚合物製成的薄膜，熱壓該薄膜而製成的。
8. 一種單面金屬箔層疊體，其特徵為，它是利用申請專利範圍第 6 項所述的製造方法得出的。
9. 如申請專利範圍第 8 項之單面金屬箔層疊體，其中可以形成單面金屬箔層疊體的光學各向異性的熔融相的聚合物層厚度在 15 微米以下。
10. 如申請專利範圍第 8 項之單面金屬箔層疊體，其中可以形成光學各向異性熔融相的聚合物層的分子定向度在 1.3 以下。
11. 一種單面金屬箔層疊體，其特徵為，它由可以形成厚度在 15 微米以下的光學各向異性熔融相的聚合物層，和結合在它的一個表面上的金屬箔層構成；前述聚合物層的分子定向度在 1.3 以下。
12. 一種安裝電路基板，其特徵為，它利用如申請專利範圍第 8 至 11 項中任一項所述的單面金屬箔層疊體，將電子元件安裝在該層疊體上，並與層疊體連接。
13. 一種多層安裝電路基板，其特徵為，它利用將該層疊體或其它層疊體，與如申請專利範圍第 8 至 11 項中任一項所述的單面金屬箔層疊體重合構成的多層層疊體，將電子元件安裝在該多層層疊體上，並與該多層層疊體連接。

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## 六、申請專利範圍

14. 一種兩面金屬箔層疊體的製造方法，其特徵為，將金屬箔與如申請專利範圍第 8 至 11 項中任一項所述的前述單面金屬箔層疊體的前述聚合物層重合，進行熱壓來製造兩面金屬箔層疊體。
15. 一種兩面金屬箔層疊體，其特徵為，它利用如申請專利範圍第 14 項所述的製造方法得出的。
16. 一種單面金屬箔層疊體的製造裝置，其特徵為，它具有熱壓裝置和分割裝置；該熱壓裝置可以將夾在兩塊層狀金屬箔之間，用可以形成光學各向異性熔融相的聚合物製成的薄膜，在厚度方向進行熱壓；該分割裝置可以將能形成光學各向異性熔融相的聚合物層及其上表面的金屬箔層，和下表面的金屬箔層通過熱壓形成的兩面金屬箔層疊體，沿前述聚合物層的厚度方向，撕開成上面和下面兩個層疊體。

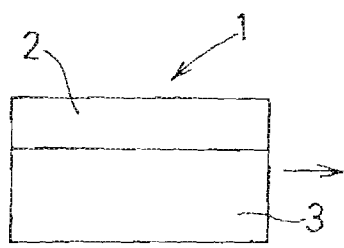
(請先閱讀背面之注意事項再填寫本頁)

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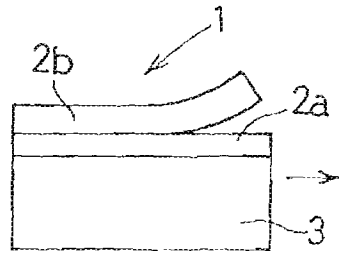


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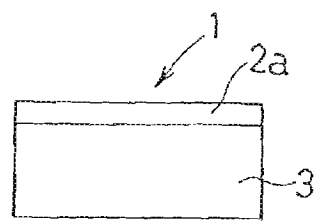
第1圖a



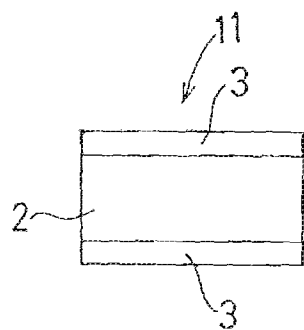
第1圖b



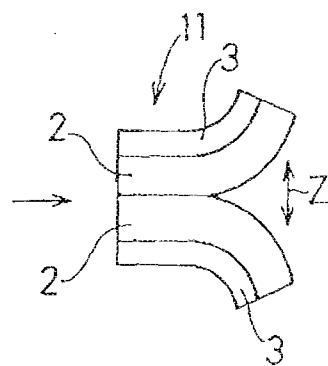
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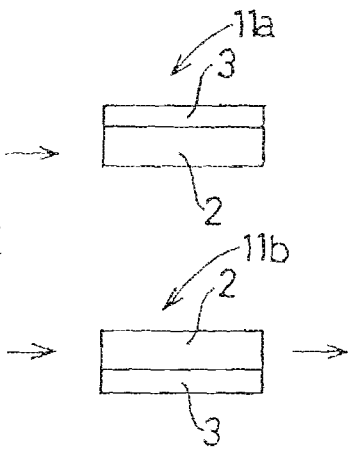
第2圖a



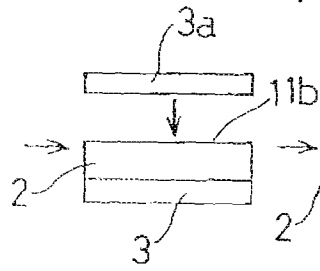
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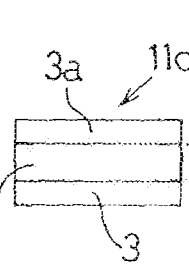
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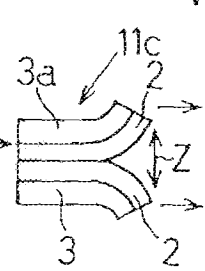
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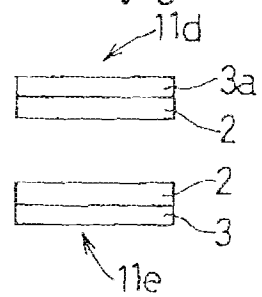
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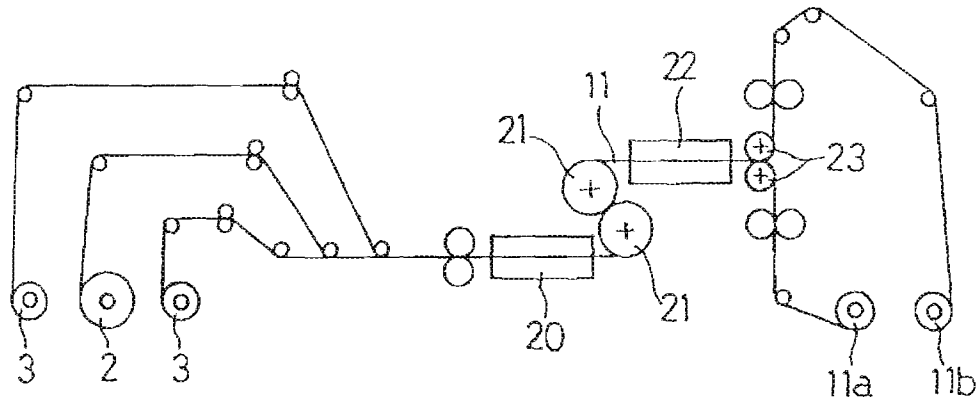
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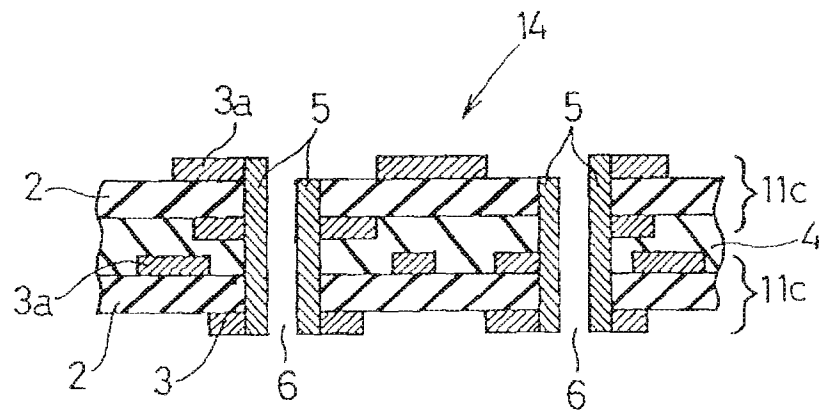
第2圖g



第3圖



第5圖



第6圖

